

# **Acid Separation from Bio-Oil Using Ionic Liquid**

by

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

MAY 2012

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# CERTIFICATION OF APPROVAL

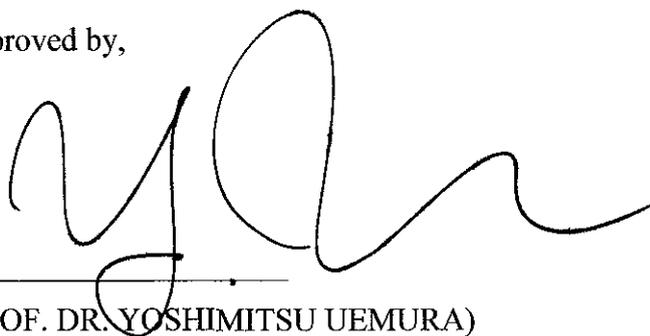
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A project dissertation submitted to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
in partial fulfilment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)

Approved by,



A handwritten signature in black ink, consisting of a large, stylized 'Y' followed by a large 'U' and a long horizontal stroke ending in a small wave.

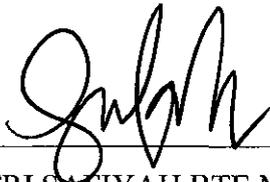
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UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK

May 2012

## 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.



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(PUTRI SAFIYAH BTE MEGAT MAZHAR KHAIR)

## ABSTRACT

Studies on reducing the high acid concentration in bio-oil using ionic liquid as a new separation method needs to be conducted. Organic acid that contains in bio-oil supposed to be able to be extracted using two types of ionic liquid which are 1-butyl-3-methylimidazolium thiocyanate [Bmim][SCN] and 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][OTf]. Studies on bio-oil upgrading are necessary in order to improve its efficiency as an alternative fuel and to put it on par with fossil fuel as the world is approaching towards a “greener” source of energy. The objective of this project is mainly to study the acid separation from bio-oil using two types of ionic liquids which are [Bmim][SCN] and [Bmim][OTf] by analysing the amount of acetic acid after the separation in both upper and lower phase of liquids that are formed using Gas Chromatography (GC). The methodology for this project consists of extraction procedure and analysis of the amount of acetic acid after extraction using GC-Flame Ionization Detector. Findings show that the ionic liquid are able to extract acetic acid contains in bio-oil however it will also extract other components, like phenol, hence prohibiting two phase separation.

## ACKNOWLEDGEMENT

Firstly, I am especially grateful to Allah, because without his love and blessings, I wouldn't be able to finish this final year project or even partake in this. I am heartily thankful to my supervisor, Prof. Dr. Yoshimitsu Uemura, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding in this project, in the hopes of becoming a well-rounded chemical engineer. Besides, I would love to thank Ms Hafizah Afif for her exceptional motivation and guidance for me to develop and complete this project. I would also love to thank Assoc. Prof. Dr. Zakaria B Man and Ms Hasiyah Kamaruddin, fellow PETRONAS Ionic Liquid Centre members for helping me in initiating and adapting to this project. Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the final year project. Thank you.

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# CHAPTER 1 : INTRODUCTION

## 1.1 Background Study

Bio-oil is an unstable mixture with high composition of oxygenated molecules which are also viscous and corrosive produced from biomass feedstock through the pyrolysis process. It appears to be black or dark red-brown or dark green, depending on the original feedstock and the variability during the pyrolysis process. It also has lower heating value compared to petroleum liquid because of its high oxygen content. For a typical pyrolysis process, the bio-oil produced contains high concentration of acetic acid ( $pK_a = 4.76$ ), one of the carboxylic acids. Acid removing from bio-oil is necessary in order to diminish the corrosiveness of bio-oil and also to reduce the instability of bio-oil due to the reactivity of oxygenated groups. With the bio-oil upgrading, higher heating value could possibly be obtained and leads to a more practicable usage of green fuels in the future.

On the other hand, ionic liquid is also known as “designer solvents” due to various possible combinations of cation and anion in order to obtain the suitable solvent depending on a specific application. It can be made to according to certain application with appropriate physicochemical properties. Aside from that, it was once known to be a “green solvent” due to its recyclability. The application of the solvent in a specific process could improve the efficiency of the process and the production cost. There have been some studies on acid extraction using ionic liquid from crude oil and bio-production processes which are proven success. However, it is yet to be proven whether ionic liquid could successfully separate acid from bio-oil.

Studies on acid separation from bio-oil using ionic liquid is deemed to be relevant since it could possibly contributes to the development of biofuel technology especially in Malaysia, since there are abundance of biomass feedstock available. In order to use bio-oil commercially as an alternative fuel, studies on bio-oil upgrading is necessary so that, the corrosiveness of bio-oil could be reduced and hence it is suitable to be used in engines for a long period of time. Aside from alternative fuel, bio-oil has also been considered to as sources of raw material for various industrial chemical. However, the content of organic acid in bio-oil has caused a problem

especially in corrosion of metals and storage instability. Upgraded bio-oil could be the solution to these kinds of problems.

For this project, acid separation from bio-oil using ionic liquid is going to be observed through experimental procedures that consist of extraction process and characterization of bio-oil before and after extraction. Because of that, the project is appeared to be timely feasible for 8 months duration of final year project determined by the university. Aside from that, all of the equipments needed are available inside the university.

## **1.2 Problem Statement**

Studies on reducing the high acid concentration in bio-oil using ionic liquid as a new separation method needs to be conducted. Organic acid that contains in bio-oil supposed to be able to be extracted using two types of ionic liquid which are 1-butyl-3-methylimidazolium thiocyanate [Bmim][SCN] and 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][OTf].

Studies on bio-oil upgrading are necessary in order to improve its efficiency as an alternative fuel and to put it on par with fossil fuel as the world is approaching towards a “greener” source of energy.

## **1.3 Objective and Scope of Study**

The objectives of this project include:

1. To study the acid separation from bio-oil using two types of ionic liquids which are [Bmim][SCN] and [Bmim][OTf]
2. To observe the acid separation as a formation of two liquid phases
3. To analyse the amount of acetic acid after the separation in both upper and lower phase of liquids that are formed using Gas Chromatography

For this project, the types of bio-oil used are K4K6 which consists of 67% water content; K2 with 0.18% water content; Dried K4K6 where a drying agent, sodium sulfate is used to remove all water content; emulated bio-oil (EBO)1 which consists of four major components is bio-oil that is 68% of phenol, 16% of acetic acid, 11% of furfural and 5% of p-cresol; EBO2 which is a mixture of 0.5% phenol in hexane; EBO3, EBO4, EBO5 and EBO6 which are a mixture of 0.5, 2, 5 and 10% acetic acid in hexane, respectively. These bio-oils are mixed with ionic liquid [Bmim][SCN]

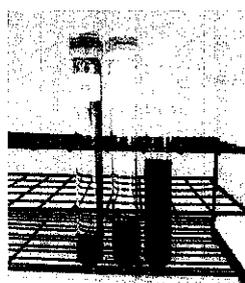
and/or [Bmim][OTf] at different mixing speeds and temperatures and left to settle. Gas Chromatography analysis is done when there is formation of two immiscible liquids for both phases.

## CHAPTER 2 : LITERATURE REVIEW

Demirbas (2011) tabulated the typical properties and characteristic of wood derived bio-oil as shown in Table 2.1 to further explain about bio-oil:

**Table 2.1: Typical Properties and Characteristics of Wood-Derived Bio-Oil**

<b>Property</b>	<b>Characteristic</b>
<b>Appearance</b>	From almost black or dark red-brown to dark green, depending on the initial feedstock and the mode of fast pyrolysis



**Figure 2.1: Physical Appearance of Bio-oil**

<b>Miscibility</b>	<ul style="list-style-type: none"> <li>• Varying quantities of water exists, ranging from ~15 wt% to an upper limit of ~30-50 wt% water, depending on production and collection.</li> <li>• Pyrolysis liquid can tolerate the addition of some water before phase separation occurs</li> <li>• Bio-oil can't be dissolved in water</li> <li>• Miscible with polar solvents such as methanol and acetone but totally immiscible with petroleum-derived fuels</li> </ul>
<b>Density</b>	Bio-oil density is ~1.2 kg/L, compared to ~0.85 kg/L for light fuel oil
<b>Viscosity</b>	Viscosity of bio-oil varies from as low as 25 cSt to as high as 1000 cSt (measured at 313 K) depending on the feedstock, the water content of the oil, the amount of light ends that have collected, the pyrolysis process used and the extent to which the oil has been aged
<b>Distillation</b>	<ul style="list-style-type: none"> <li>• It cannot be completely vaporized after initial condensation from the vapour phase at 373 K or more, it rapidly reacts and eventually produces a solid residue from ~50 wt.% of the original liquid</li> <li>• It is chemically unstable, and the instability increases with heating</li> <li>• It is always preferable to store the liquid at or below room temperature; changes do occur at room temperature, but much more slowly and they can be accommodated in a commercial application</li> </ul>
<b>Ageing of pyrolysis liquid</b>	<ul style="list-style-type: none"> <li>• Causes unusual time dependent behaviour</li> <li>• Properties such as viscosity increases, volatility increases, phase separation and decomposition of gums change with time</li> </ul>

Facts obtained from Demirbas (2011) as stated in Table 2.1 above is useful for further understanding of properties of bio-oil. Different properties of bio-oil would give out different result later on with the experiment. Since bio-oil to be used in this experiment could also be different with one another, the most suitable bio-oil to be used for this experiment is those with low water content. It is to observe the extractability of acid from oil part of the bio-oil itself.

Bio-oil is significantly different from petroleum fuels due to its very high viscosity, moisture content and a lower heating value. Unlike petroleum fuels that form naturally under the ground, bio-oil is a product of converting biomass through pyrolysis process, which is a thermal decomposition that occurs in the absence of oxygen. The bio-oil formed at 725 K contains high concentration of acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimethoxyphenol and 2-cyclopenten-1-one, and so on, with a high percentage of methyl derivatives (Demirbas, 2011). Based on Demirbas (2011) statement, the targeted organic acid to be removed from bio-oil for this project is acetic acid because it widely constitutes in the bio-oil. Later on the part for characterization of bio-oil, analysis on acetic acid should be emphasised.

According to (Demirbas, 2011), bio-oil contains high concentration of acetic acid, along with many other methyl derivatives. Based on his paper, it is suggested that the study on the deoxygenation of bio-oil is very much needed.

There are some studies that successfully measured the properties of upgraded bio-oil. The following Table 2.2 shows the comparison between raw and upgraded bio-oil (Demirbas, 2011):

**Table 2.2: Properties of the raw and upgraded bio-oil**

<b>Property</b>	<b>Raw bio-oil</b>	<b>Upgraded bio-oil</b>
<b>Density</b>	1.12	0.93
<b>Elemental analysis (wt. %)</b>		
<b>C</b>	60.4	87.7
<b>H</b>	6.9	8.9
<b>O</b>	41.8	3.0
<b>N</b>	0.9	0.4
<b>Heating Value (MJ/kg)</b>	21.3	41.4

Based on Table 2.2, it is obvious that the properties between raw and upgraded bio-oil is different. The properties of upgraded bio-oil achieved are due to the hydrodeoxygenation (HDO) process. The reaction involves removing bound oxygen in the form of water. The HDO process is one established process for bio-oil upgrading.

Oliveira, Grande, & Rodrigues (2009) stated that

Diversity of anion–cation combinations, diversity of modes of preparation, modes of purification and nature of impurities (quality), diversity of properties, diversity of mode of use, diversity of applications. This is one of the reasons why it is so difficult to make generalisations about their physical properties or their use. (p.3).

From their statement above, there are two things that could be concluded about ionic liquid, which are:

- Different anion-cation combination could be functional in different application, in which that specific type of combination could be able to extract the organic acid from bio-oil.
- Due to that diversity, properties of ionic liquids could not be easily generalized.

Opportunately, BASF has announced the development of a new process called BASIL (Basic Acid Scavenging utilising Ionic Liquid) to improve the acid trapping in a more convenient way (Oliveira, Grande, & Rodrigues, 2009). From their work, it is identified that 1-methylimidazolium as a nucleophilic catalyst which is efficiently used as acid scavenging especially in multi-ton scale processes by BASF. According to Oliveira, Grande, & Rodrigues (2009), the anion of ionic liquids play a fundamental role, where the acidity levels are in order:  $[\text{PF}_6]^- > [\text{BF}_4]^- > [\text{NTf}_2]^- > [\text{OTf}]^-$  thus implying that the basicity of the anions are in reverse order. The two types of ionic liquids provided are both contains 1-butyl-3-methylimidazolium  $[\text{BMIM}]^+$  cation, with thiocyanate  $[\text{SCN}]^-$  and trifluoromethanesulfonate  $[\text{OTf}]^-$  anion. Based on Oliveira, Grande, & Rodrigues (2009), both ionic liquids are predicted to be suitable for extracting acid from bio-oil. Figures 2.1 – 2.5 below illustrate the two ionic liquids' molecular structure:

Table 2.3: Provided Ionic Liquids for this Project

1-butyl-3-methylimidazolium thiocyanate	1-butyl-3-methylimidazolium trifluoromethanesulfonate
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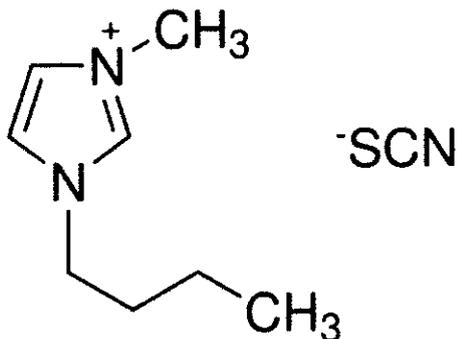


Figure 2.2: Molecular Structure of 1-butyl-3-methylimidazolium thiocyanate

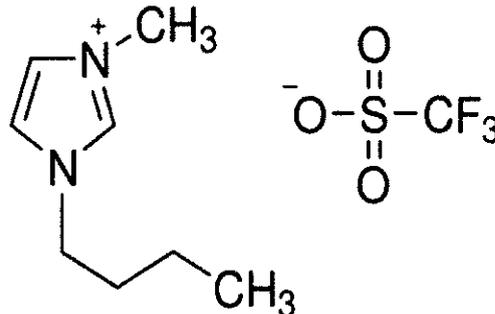


Figure 2.3: Molecular Structure of 1-butyl-3-methylimidazolium trifluoromethanesulfonate

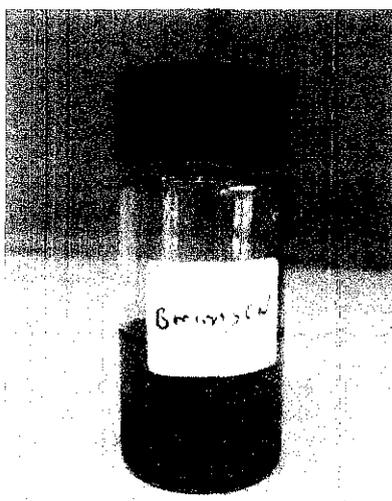


Figure 2.4: Physical View of 1-butyl-3-methylimidazolium thiocyanate

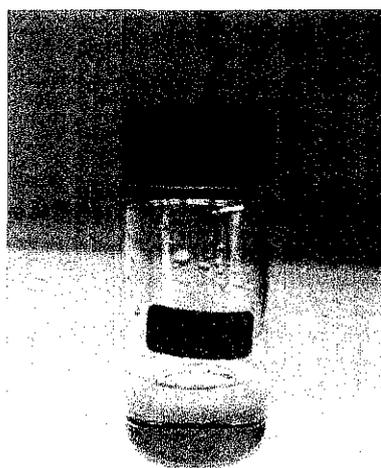
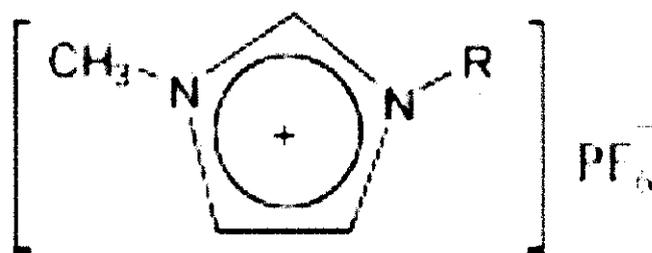


Figure 2.5: Physical View of 1-butyl-3-methylimidazolium trifluoromethanesulfonate

Previous studies shows that ionic liquid is able to extract organic acid from the fermentation of lactate by bacteria called *L. rhamnosus* using imidazolium based ionic liquid (Matsumoto, Kochiduki, Fukunishi, & Kondo, 2007). The molecular structure of the ionic liquid is as shown in Figure 2.6:



**Figure 2.6: Imidazolium-based Ionic Liquids.** R = C<sub>4</sub>H<sub>9</sub>: [Bmim][PF<sub>6</sub>]; C<sub>6</sub>H<sub>13</sub>: [Hmim][PF<sub>4</sub>]; C<sub>8</sub>H<sub>17</sub>: [Omim][PF<sub>4</sub>]

However, the study found out that the extractability of organic acid using imidazolium-based ionic liquids without any extractant is very low. The study also found out that extraction behaviours of lactic acid with imidazolium-based ionic liquids containing tri-n-butylphosphate (TBP) extractant are similar to those of conventional organic solvents, in which it needs an additional solvent for the extraction to be successful. In this study, it is understandable based on the values of distribution ratios of organic acids with ionic liquid unaided with an extractant; the extraction capacities are very low. However, the extraction that took place involved living bacteria which could possibly leads to the low extractability of organic acids.

The methodology of extraction process presented in by Matsumoto, Kochiduki, Fukunishi, & Kondo (2007) is simple and suitable to be followed for this project, where:

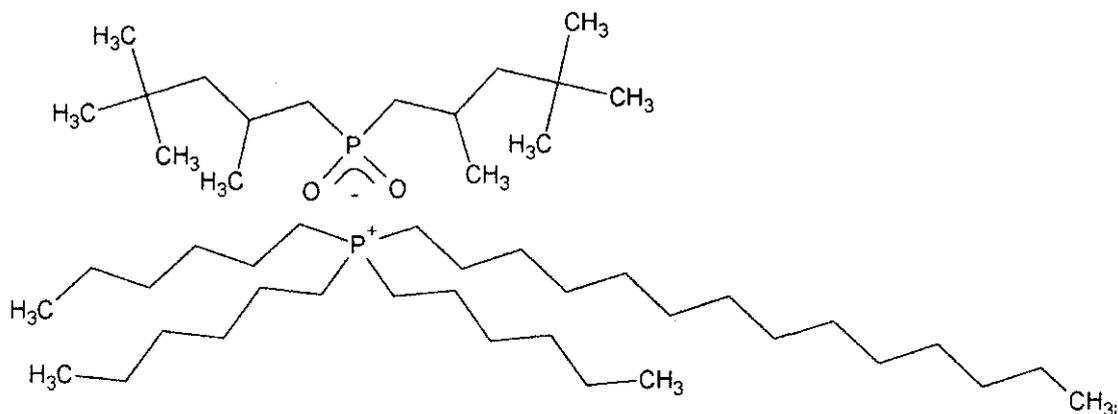
1. Both aqueous and organic solutions were mixed 20 cm<sup>3</sup> each in an Erlenmeyer flask and shaken at 303 K to reach extraction equilibrium.
2. After the two phases were separated, organic acid in the samples taken from the organic solution was stripped by 2M sodium hydroxide solution.
3. Acid concentration was determined by HPLC<sup>1</sup> while The pHs of the aqueous solutions before and after equilibration were determined by a Horiba F-12 pH meter

Matsumoto, Kochiduki, Fukunishi, & Kondo (2007) also found from the extraction of organic acids into imidazolium-based ionic liquids that the distribution constants for organic acids were relatively small, but glycolic acid (most hydrophilic acid) was not extracted at all. They also generalized the order of extractability which is Omim

<sup>1</sup>High-performance liquid chromatography

< Bmim < Hmim<sup>2</sup>. Even so, the difference of extraction capabilities of ionic liquids is relatively small.

Phosphonium ionic liquid with bis 2,4,4-trimethylpentylphosphinate anion on the other hand is proven to be an effective extractant of lactic acid with distribution coefficient above 40 (Mart'ak & Schlosser, 2007). The molecular structure of the ionic liquid is illustrated as Figure 2.7 below:



**Figure 2.7: Structure of trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate (Cyphos IL-104).**

However, with increasing acid concentration the value of distribution coefficient decreases, where the extraction will be less effective with high acid concentration. Due to this, this ionic liquid might not be very effective if the concentration of acid in bio-oil is very high. Still, the concentration of acid in bio-oil is yet to be determined. In Mart'ak & Schlosser (2007) work, they conduct the phase separation between two immiscible liquids by centrifugation, in which the liquids would be separated more efficiently compared to gravity settling.

An exploratory study on the removal of acetic and formic acid from bio-oil using calcium oxide has also been done (Sukhbaatar, Steele, Ingram, & Kim, 2009). Based on their study, 10.92% of organic acid content in bio-oil has been successfully reduced up to 1.9% of acetic acid. In their study, gas chromatography/mass spectrometry (GC/MS) analysis was done to analyse the content of raw and treated bio-oil. From their study, the methods for conducting the GC/MS could be used for analysing the before and after mixing bio-oil and ionic liquid for this project. They injected 1.4 $\mu$ L

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<sup>2</sup>Three ionic liquids were prepared namely the hexafluorophosphates of 1-butyl-3-methyl imidazolium ([Bmim][PF<sub>6</sub>]), 1-hexyl-3-methyl imidazolium ([Hmim][PF<sub>6</sub>]) and 1-octyl-3-methyl imidazolium ([Omim][PF<sub>6</sub>])

of 2-5% solution diluted in methanol with temperature of 270 °C with oven temperature of 280 °C and it was run for about 67 minutes. For this project, such method is applicable, however, the 67 minutes of run time is a little bit long. Sukthbaatar, Steele, Ingram & Kim (2009), however underwent their mixing process with quite high amount of material which is 50 g of each bio-oil and methanol.

Bio-oil characterization from different feedstock of wet and moisture free (mf) palm empty fruit bunch (PEFB) and pinewood has been conducted and the result of the ultimate analysis are given in the following Table 2.4 (Pimenidou & Dupont, 2012):

**Table 2.4: Characteristics of the bio-oils and numerical indicators for their utilisation or upgrading.**

Analysis oil	'Wet' pine	'Wet' PEFB	mf pine	mf PEFB
<b>Ultimate</b>				
C (wt.-%-mol fr)	40.75–0.257	45.23–0.284	52.76–0.359	59.98–0.409
H (wt.-%-mol-fr)	6.59–0.494	6.53–0.488	5.29–0.427	5.08–0.412
N (wt.%) (mol fr)	$1.4 \times 10^{-3}$ – $7.6 \times 10^{-4}$	$8.5 \times 10^{-3}$ – $4.6 \times 10^{-3}$	$1.8 \times 10^{-3}$ – $1.1 \times 10^{-3}$	$11.3 \times 10^{-3}$ – $6.6 \times 10^{-3}$
S (wt.%) (mol fr)	$0.0436$ – $1.03 \times 10^{-4}$	$0.0611$ – $1.4 \times 10^{-4}$	$0.0564$ – $1.44 \times 10^{-4}$	$0.0810$ – $2.07 \times 10^{-4}$
K (wt.%) (mol fr)	$0.00575$ – $1.1 \times 10^{-5}$	$0.14176$ – $2.74 \times 10^{-4}$	$0.00744$ – $1.53 \times 10^{-5}$	$0.18801$ – $3.94 \times 10^{-4}$
Na (wt.%) (mol fr)	$0.00793$ – $2.61 \times 10^{-5}$	$0.00745$ – $2.45 \times 10^{-5}$	$0.01027$ – $3.64 \times 10^{-5}$	$0.00988$ – $3.52 \times 10^{-5}$
Ca (wt.%) (mol fr)	$0.04$ – $7.6 \times 10^{-5}$	$0.05$ – $9.4 \times 10^{-5}$	$0.0518$ – $1.06 \times 10^{-4}$	$0.0663$ – $1.34 \times 10^{-4}$
Si (wt.%) (mol fr)	$0.0564$ – $1.52 \times 10^{-4}$	$0.0523$ – $1.41 \times 10^{-4}$	$0.0730$ – $2.12 \times 10^{-4}$	$0.0694$ – $2.03 \times 10^{-4}$
O (wt.-%-mol-fr)	52.27–0.247	47.03–0.222	41.72–0.213	33.72–0.173
<b>Proximate</b>				
Water (wt.%)	22.55	24.30	0	0
Volatiles (wt.%)	86.6–88.2	84.3–88.7	65.6–66.1	41.3–60.0
Carbon (wt.%) rsd	11.8–13.4	11.3–15.7	33.9–34.4	40–58.7
Ash (wt.%)	3.78	2.43	4.89	3.22
HHV (MJ/kg) b.c.	15.6	19.8	20.14	26.18
HHV (MJ/kg) Zhu	14.53	16.99	23.4	27.6
HHV (MJ/kg) Chan	16.5	18.5	20.3	23.4
LHV (MJ/kg) bc	14.2	18.4	19.0	25.1
H <sub>f</sub> 25°C (MJ/kg) b.c.	-38.3	-43.9	-44.9	-53.0
<b>Numerical indicators</b>				
Max H <sub>2</sub> yield (wt.%)	13.7	15.9	17.7	21.0
(H/C) <sub>eff</sub>	-0.01	0.11	0.0	0.11
x = Ca/Si (mol fr)	0.50	0.67	0.50	0.67
Af (mol/GJ)	-1.75	-0.64	-1.69	0.58
S/(K + Na) (mol fr)	2.76	0.48	2.76	0.48

Based on the values obtained by Pimenidou & Dupont (2012), the characterization value for this project could be compared with this later.

Muhammad, et al. (2012) have been studying on the Effect of Ionic Liquid Treatment on Pyrolysis Products from Bamboo. In their study, the amount of acetic acid in bio-oil is obtained. They stated that the quality of bio-oils depends on the amount of organic acids contain in it. The effects of ionic liquids treatment on acetic acid contents are shown in Figure 2.8:

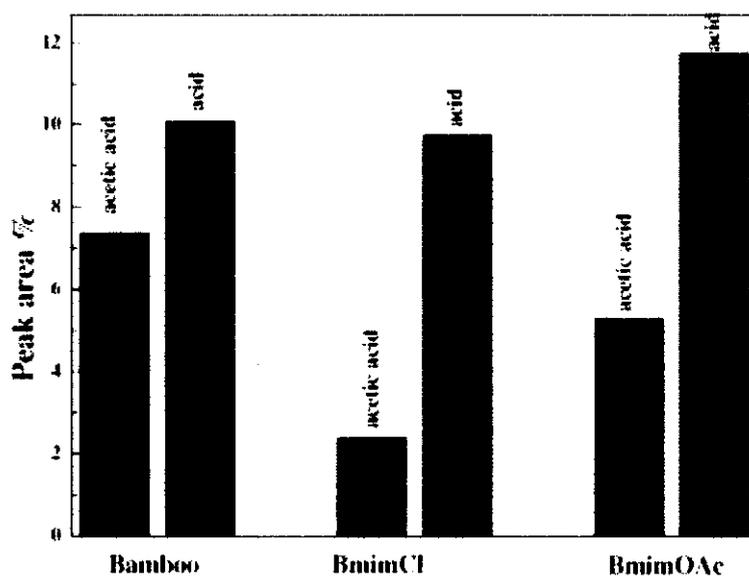


Figure 2.8: Effects of ionic liquids on the production of acetic acids and

They found that after the bio-oil is treated with ionic liquid BmimCl and BmimOAc, the amount of acetic acid contains in bamboo sample is significantly decreased. However, the total acid contents for all samples are about the same, where reduction is very small. From their findings, it is proven that ionic liquid could be used to separate acetic acid from bio-oil, but not all organic acid contain in it.

The major components of the bio-oil produces from palm kernel shell were phenol, guaiacol, syringol, dimazine, furfural and acids (Kim, Jung, & Kim, 2010). According to Kim et. al. (2010), the phenol and phenolic compound contents in the bio-oil produced from palm kernel shell were very high compared to bio-oils obtained from other biomasses. The GC-MS analysis of bio-oil produced from palm kernel shell as said by Kim et. al. (2010) is tabulated in Table 2.5:

**Table 2.5: Main compounds of the bio-oil from palm kernel shell**

<b>Components</b>	<b>Area (%)</b>
Acetic acid	5.46
Furfural	3.42
Phenol	22.1
p-Cresol	1.32
o-Guaiacol	3.00
Creosol	2.10
Catechol	3.67
3-Methoxy-1,2-benzenediol	1.64
Homocatechol	1.55
Vinylguaiacol	1.97
Syringol	4.09
Iso-eugenol	1.34
Methoxyeugenol	3.09
o-Cresol	1.07
3-Methyl-1,2-benzenediol	1.30
4-Hydroxy-benzoic acid	0.44
2-Methoxy-benzeneethanol	1.01
1,2,4-Trimethoxybenzene	4.51
Methylparaben	1.13
4-Ethyl-1,3-benzenediol	0.80
1,2,4-Benzenetriol	0.27
3-Hydroxy-benzoic acid	0.23
Propanoic acid	0.74

The analysis made by Kim et. al. (2012) can be used as reference to create an emulated bio-oil, which contains compounds that majorly comprises in the bio-oil.

## CHAPTER 3 : METHODOLOGY

### 3.1 Project Flow

Figure 3.1 shows the summary of the project sequence:

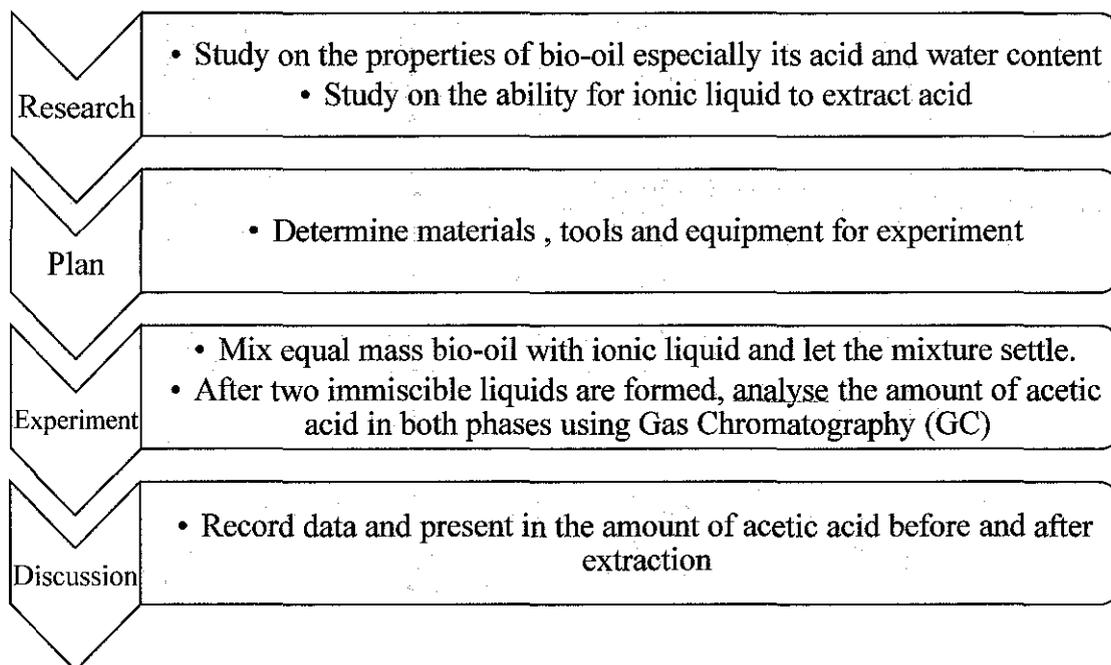


Figure 3.1: Project Flow Diagram

### 3.2 Experiment Procedure

#### 3.2.1 Extraction Process

The process is done with small amounts of material following a typical procedure. There are 12 runs are done according to different parameters. For the first run, at room temperature, 6 g of bio-oil and 6 g of ionic liquid is mixed and stirred using a magnetic stirrer at rotation speed of 500 rpm for one hour and left to settle for 3 hours. For the second run, the amount of bio-oil and ionic liquid is reduced to 2 g, and same procedure is repeated. Same procedure is done until the fourth run, however with different mass and type of bio-oil and ionic liquid, as shown in Table 3.3.

For the fifth run, the mixing is done in sample tubes and its speed is increased to 2500 rpm, using vortex mixer, for 5 minutes. The settling temperature is reduced to -10 °C for 24 hours. For the sixth run onwards, the mixing and settling parameters is

done same like 5<sup>th</sup> run, but the settling temperature is done in room temperature. The formation of two immiscible liquids is observed for each run. If the formation of two immiscible is observed, the two liquids are separated using glass pipette, before proceeding with the analysis. Table 3.3 summarizes the different parameters used in each run of extraction process, until run number 12.

### 3.2.2 Drying of Bio-oil K4K6

Sodium sulphate anhydrous (Na<sub>2</sub>SO<sub>4</sub>) is used to dry the bio-oil K4K6, due to its high water content. The indication that is when the water is still contained in the bio-oil is when the sodium sulphate is clumped together. Sodium sulphate is continuously added until the sodium sulphate will remain loose and granular, indicating that the bio-oil is already dried. For this drying, the parameters are tabulated as in Table 3.1:

**Table 3.1: Mass in Drying Bio-oil Procedure**

<b>Component</b>	<b>Mass (g)</b>
Bio-oil K4K6	4.3020
Sodium Sulphate	4.1673

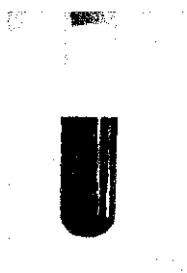
### 3.2.3 Emulated Bio-oil 1 (EBO 1)

Due to incapability of the original bio-oil to produce two immiscible liquids after being mixed with ionic liquid, EBO 1 is created by mixing the following component as shown in Table 3.2:

**Table 3.2: Mass in Producing Emulated Bio-oil 1**

<b>Component</b>	<b>Mass (g)</b>	<b>Percentage (%)</b>
Phenol	71.2832	68.25%
Acetic Acid	16.9730	16.25%
Furfural	11.1111	10.64%
P-Cresol	5.0722	4.86%

Figure 3.2 below shows the resulting EBO 1:



**Figure 3.2: Emulated Bio-oil**

Table 3.3: Summary of Parameters for Extraction Process

Run	Bio-oil /Mixture	Mass bio-oil /mixture (g)	Ionic Liquid	Mass ionic liquid (g)	Temperature (°C)	Mixing Speed (rpm)	Mixing Time (minute)	Settling Time (hour)
1	K4K6	6.0000	Bmim OTf	6.0000	24	500	60	3
2	K4K6	2.0001	Bmim SCN	2.0001	24	500	60	3
3	K2	1.1101	Bmim SCN	1.1151	24	500	60	3
4	Dried K4K6	2.0068	Bmim OTf	2.5955	24	500	60	3
5	K4K6	1.0219	Bmim OTf	1.0328	-10	2500	5	24
6	EBO <sup>3</sup> 1 <sup>4</sup>	1.2970	Bmim SCN	1.2167	24	2500	5	24
7	EBO 1	1.1717	Bmim OTf	0.9438	24	2500	5	24
8	EBO 2 <sup>5</sup>	1.0988	Bmim SCN	1.1016	24	2500	5	24
9	EBO 3 <sup>6</sup>	1.0684	Bmim SCN	1.085	24	2500	5	24
10	EBO 4 <sup>7</sup>	1.0905	Bmim SCN	0.9337	24	2500	5	24
11	EBO 5 <sup>8</sup>	1.0311	Bmim SCN	0.9172	24	2500	5	24
12	EBO 6 <sup>9</sup>	1.0016	Bmim SCN	0.9166	24	2500	5	24

<sup>3</sup> EBO: Emulated Bio-Oil

<sup>4</sup> 68% phenol, 16% acetic acid, 11% furfural, 5% p-cresol

<sup>5</sup> 0.5% Phenol in Hexane

<sup>6</sup> 0.5% Acetic Acid in Hexane

<sup>7</sup> 2% Acetic Acid in Hexane

<sup>8</sup> 5% Acetic Acid in Hexane

<sup>9</sup> 10% Acetic Acid in Hexane

### 3.2.4 Emulated Bio-oil 2 (EBO 2)

Since EBO 1 resulting in good miscibility with ionic liquid, EBO 2 is made where 0.5% of phenol, one of the main components in bio-oil, is mixed with hexane, a nonpolar molecule. The mixture is mixed according to Table 3.4:

Table 3.4: Mass in Producing Emulated Bio-oil 2

Component	Mass (g)	Percentage (%)
Hexane	2.0767	99.29%
Phenol	0.0149	0.71%
Total	2.0916	100.00%

### 3.2.5 Emulated Bio-oil 3, 4, 5 and 6 (EBO 3, 4, 5 and 6)

Unlike EBO 2, EBO 3 until 6 is made by mixing a portion of acetic acid, with hexane according to Table 3.5:

Table 3.5: Mass in Producing Emulated Bio-oil 3, 4, 5 and 6

EBO	Concentration (%)	Mass Acetic Acid (g)	Mass Hexane (g)	Total Mass (g)
3	0.52%	0.0056	1.0628	1.0684
4	2.00%	0.0218	1.0687	1.0905
5	5.17%	0.0533	0.9778	1.0311
6	10.27%	0.1029	0.8987	1.0016

### 3.2.6 Gas Chromatography Analysis

This analysis was done when immiscible two liquid phases are formed in each run. After the two liquid phases were separated, about 0.3 g of sample from each phase was taken and mixed with propanol, as the internal standard. 0.4  $\mu$ L of each mixture was then injected to Shimadzu's GC-2014 with flame ionization detector (FID). Concentration of the target component was calculated from the gas chromatogram data using the internal standard method.

Two calibration curves are made which are phenol-propanol and acetic acid-propanol. Table 3.6 shows the parameters taken to produce phenol-propanol calibration curve, where  $M_P$  is the mass of phenol,  $M_{IS}$  is the mass of internal standard which is propanol, while  $A_P$  is the area under the peak curve of gas chromatogram data for internal standard which is phenol,  $A_{IS}$  is the area under the peak curve of gas chromatogram data for internal standard which is propanol and  $C$  is the mass percentage of phenol in propanol:

Table 3.6: Phenol-Propanol Calibration Curve

$M_P$ (g)	$M_{P+IS}$ (g)	$M_{IS}(g)$	C (%)	$A_P$	$A_{IS}$	$M_P/M_{IS}$	$A_P/A_{IS}$
0.0016	1.2425	1.2409	0.13	61211	39559416	0.0013	0.0015
0.0032	1.3291	1.3259	0.24	123626	40155650	0.0024	0.0031
0.0084	1.2248	1.2164	0.69	77592	10002359	0.0069	0.0078
0.0100	1.2916	1.2816	0.77	404856	36230429	0.0078	0.0112
0.0222	1.3164	1.2942	1.69	1048138	42719465	0.0172	0.0245

Figure 3.3 shows the graph after plotting  $A_P/A_{IS}$  against  $M_P/M_{IS}$  for the calibration curve. The equation for best linear fitting the curve obtained is  $A_P/A_{IS} = 1.4553 M_P/M_{IS} - 0.0007$ .

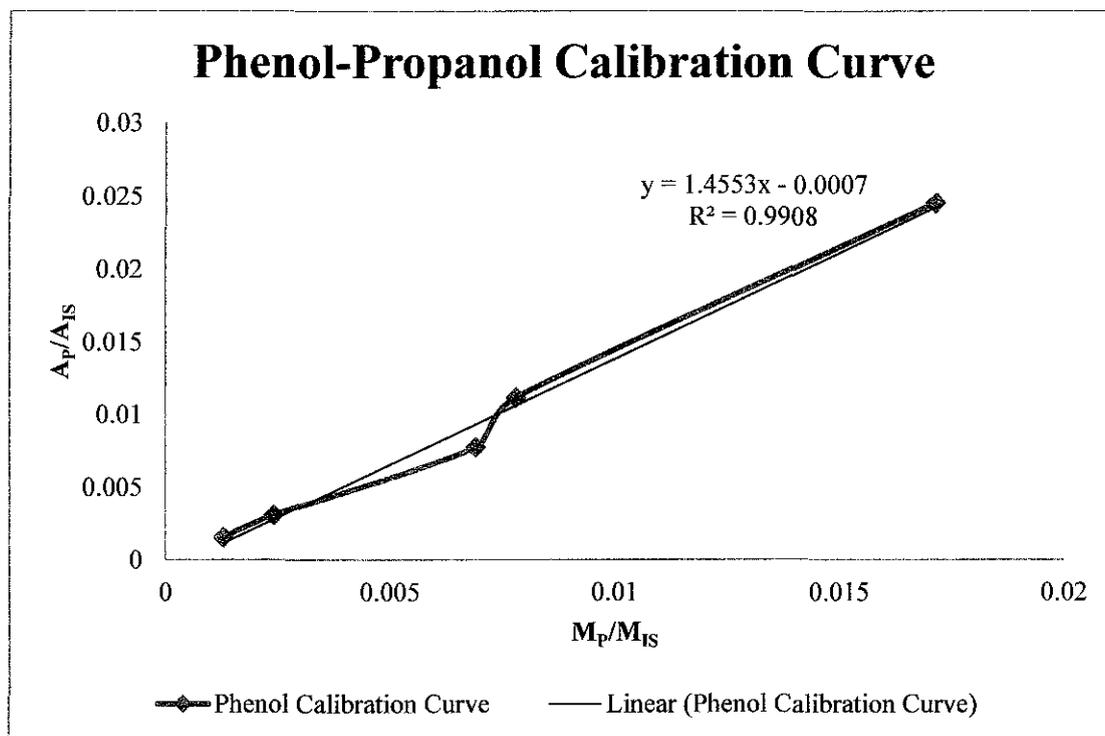


Figure 3.3: Phenol-Propanol Calibration Curve

The other calibration curve made is acetic acid-propanol curve, in order to calculate the amount of acetic acid contain in upper and lower phase after extraction process. Table 3.7 shows the parameters taken to produce acetic acid-propanol calibration curve, where  $M_A$  is the mass of phenol,  $M_{IS}$  is the mass of internal standard which is propanol, while  $A_A$  is the area under the peak curve of gas chromatogram data for internal standard which is phenol,  $A_{IS}$  is the area under the peak curve of gas chromatogram data for internal standard which is propanol and C is the mass percentage of acetic acid in propanol:

Table 3.7: Acetic Acid-Propanol Calibration Curve

$M_A$ (g)	$M_{A+IS}$ (g)	$M_{IS}(g)$	C (%)	$A_A$	$A_{IS}$	$M_A/M_{IS}$	$A_A/A_{IS}$
0.0069	1.5433	1.5364	0.45	60880	61237605	0.0045	0.0010
0.0325	1.1388	1.1063	2.85	653500	59755710	0.0293	0.0109
0.0498	0.9012	0.8514	5.53	1315947	56284187	0.0585	0.0234
0.1095	0.8334	0.7239	13.14	3504956	54650483	0.1513	0.0641

Figure 3.4 shows the graph after plotting  $A_A/A_{IS}$  against  $M_A/M_{IS}$  for the calibration curve. The equation for best linear fitting the curve obtained is  $A_A/A_{IS} = 0.4323 M_A/M_{IS} - 0.0015$ .

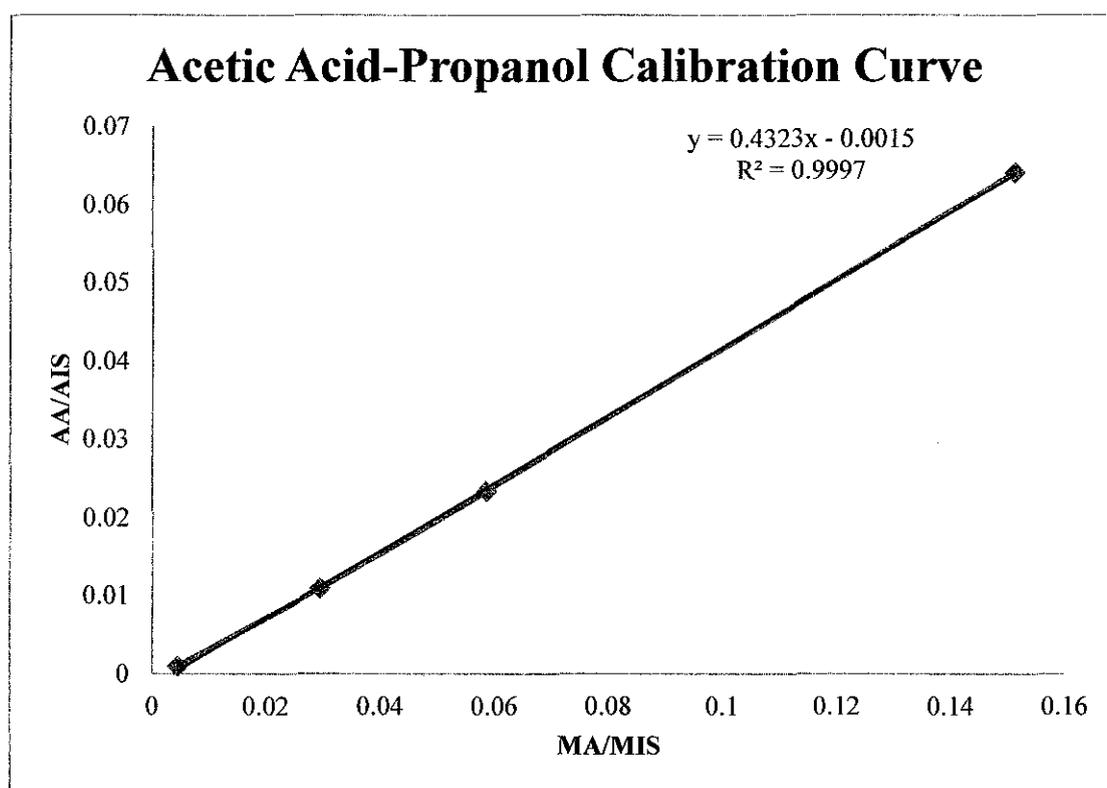


Figure 3.4: Acetic acid-Propanol Calibration Curve

The calibration equation obtained for both curves will later be used to determine the amount of component contain in upper or lower liquid phase after extraction.

### 3.2.7 Water Content Analysis

This analysis is done using equipment Karl Fischer titrator with volumetric titration method.

### 3.3 Gantt chart and Key Milestone

Gantt chart for the project is prepared in order to illustrate the project schedule and important key milestone. The chart is shown in Table 3.8:

Table 3.8: Gantt Chart and Key Milestone

No	Detail\Week	1	2	3	4	5	6	7	Mid-semester Break								8	9	10	11	12	13	14	15						
1	Extraction Process																													
2	Characterization procedure																													
3	Progress Report submission																													
4	Analyzation of Results																													
5	Pre-EDX																													
7	Submission of Draft Report																													
8	Submission of Dissertation																													
9	Submission of Technical Paper																													
10	Oral Presentation																													
11	Submission of Hardbound Dissertation																													

Legend	
◆	Suggested milestone
■	Process

### 3.4 Tools

Based on design experiment mentioned above, the equipments used are:

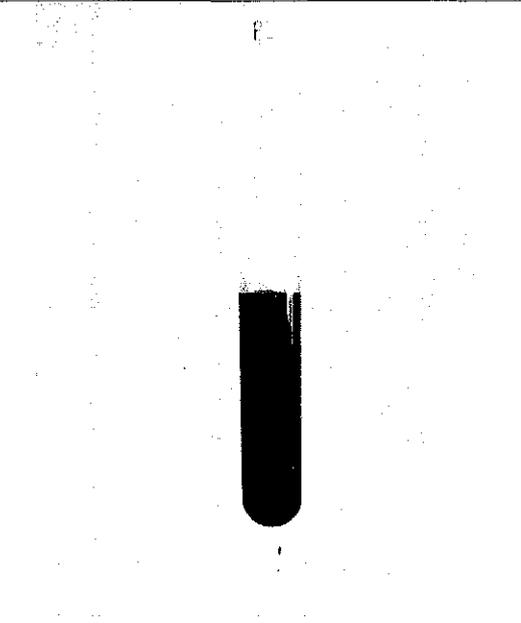
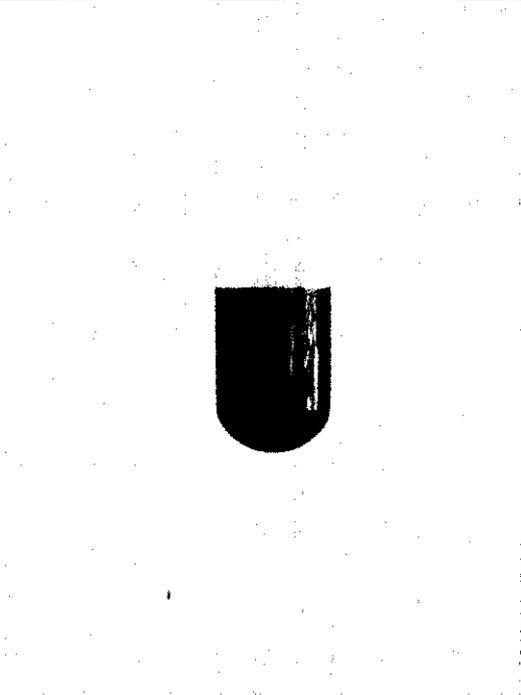
- Gas Chromatography FID analyser - Shimadzu's GC-2014
- Hotplate/Magnetic stirrer
- Vortex Mixer
- Karl Fischer titrator

## CHAPTER 4 : RESULT AND DISCUSSION

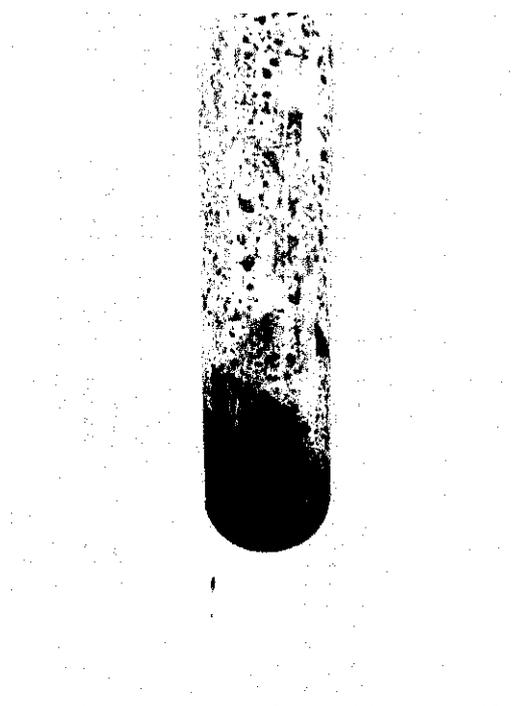
### 4.1 Physical Observation

Table 4.1 shows the observations of each runs for the extraction process:

Table 4.1: Observations of Extraction Process

Run	Observation
1	 <p>No phase separation</p>
2	 <p>No phase separation</p>

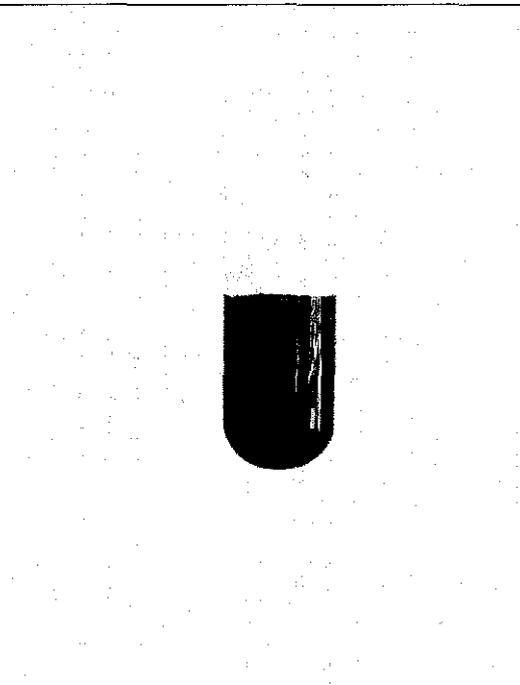
3



No phase separation

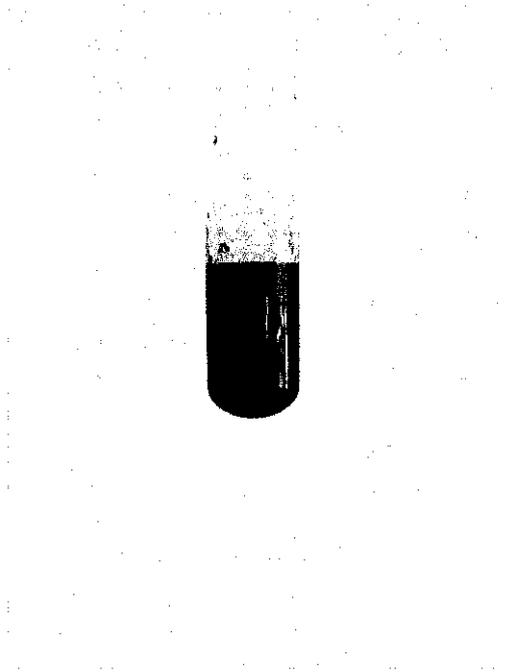
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4



No phase separation

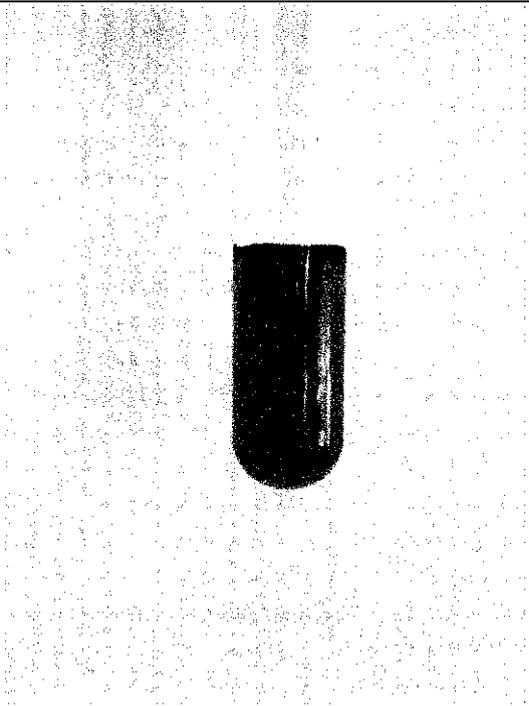
5



No phase separation

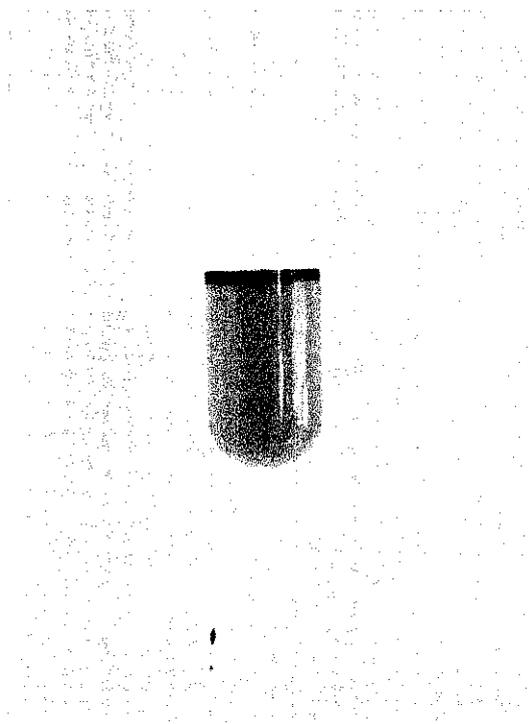
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6



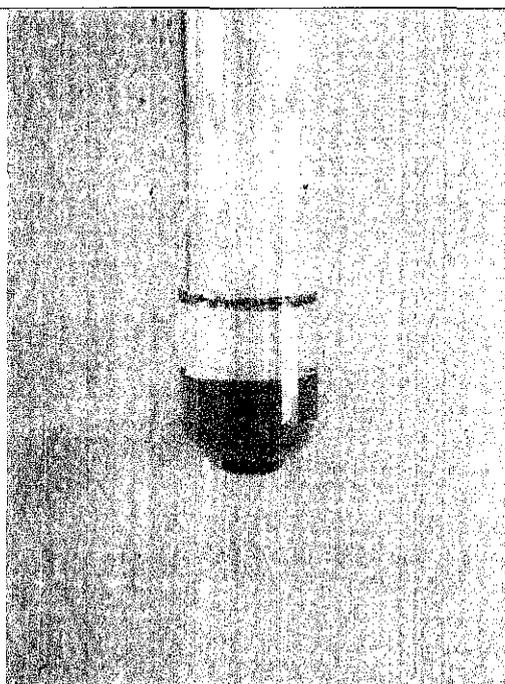
No phase separation

7



No phase separation

8-12



Formation of immiscible two liquid phases

The ionic liquids we tested have good miscibility with the bio-oil. This leads to an inappropriate combination for extraction/separation, because of their inability to produce two liquid phases. Hence, we moved out to test by creating emulated bio-oil. The formation of immiscible two liquid phases is then further analyzed using gas chromatography after both phases are separated.

## 4.2 Analysis of Upper & Lower Phase after mixing Ionic Liquid (Bmim SCN) and Phenol-Hexane

Figure 4.1 and 4.2 shows the liquids after extraction:

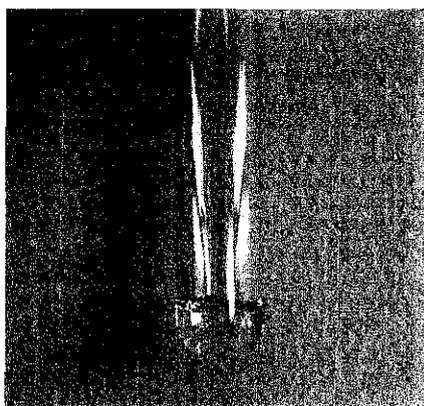


Figure 4.1: Upper Phase Liquid

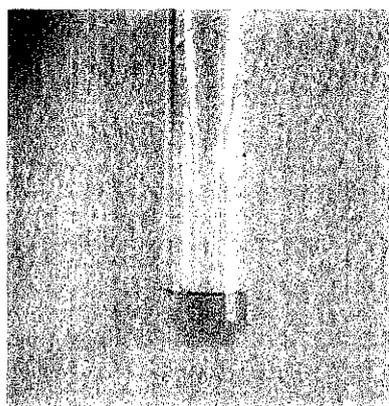


Figure 4.2: Lower Phase Liquid

Table 4.2 shows the mass of phenol, hexane and ionic liquid, Bmim SCN which are used in run 8 and also the measure mass of upper and lower phase after extraction:

Table 4.2: Analysis of Upper & Lower Phase after mixing Ionic Liquid (Bmim SCN) and Phenol-Hexane

Run	Before Extraction			After Extraction		
	Concentration (%)	Mass Phenol (g)	Mass Hexane (g)	Mass Bmim SCN (g)	Mass Upper (g)	Mass Lower (g)
8	0.71%	0.0149	2.0767	1.0555	1.9232	1.2239

The upper and lower phase is then analyzed using gas chromatograph and Table 4.3 shows the summary of the calculation of mass phenol, where  $M_s$  is mass of sample,  $M_{IS}$  is mass of propanol as the internal standard,  $T_{PhOH}$  is phenol retention time in gas chromatogram,  $A_{PhOH}$  is the area of phenol peak curve,  $A_{IS}$  is the area of internal standard and  $M_{PhOH}$  is the mass of phenol and  $M_{PhOHt}$  is total mass of phenol in lower/upper phase. All values of mass are in grams (g):

Table 4.3: Summary of The Calculation of Mass Phenol

Run	$M_s$	$M_{IS}$	$T_{PhOH}$	$A_{PhOH}$	$A_{IS}$
8 Upper	0.3835	0.3307	-	-	-
8 Lower	0.4483	0.9288	7.482	640244	52327333
Run	$A_{PhOH} / A_{IS}$	$M_{PhOH} / M_{IS}$	$M_{PhOH}$	$M_{PhOH} / M_s$	$M_{PhOHt}$
8 Upper	-	-	-	-	-
8 Lower	0.0122	0.0089	0.0083	1.84%	0.0225

To calculate the amount of component, for example, the amount of phenol in upper and lower phase, a little bit of sample is taken from the upper and lower phase respectively. As an example to show this calculation, 0.4483 g of sample from the lower phase is obtained from the total mass of lower phase as in Table 4.2 which is 1.2239 g. then, 0.3307 g of propanol is mixed into the sample as an internal standard. From the gas chromatogram data, retention time of phenol is determined to be 7.482 minutes, with a peak area of 640,244. The internal standard produced 52,327,333 peak area at its retention time 2.5 minutes. From the peak area of both phenol and internal standard, area of phenol over area of internal standard,  $A_P/A_{IS}$  is calculated to be:

$$\frac{A_P}{A_{IS}} = \frac{640,244}{52,327,333} = 0.0122$$

From equation obtained by calibration curve of phenol-propanol,  $A_P/A_{IS} = 1.4553 M_P/M_{IS} - 0.0007$ , mass phenol over mass internal standard,  $M_P/M_{IS}$  can be calculated to be:

$$\frac{M_P}{M_{IS}} = \frac{\frac{A_P}{A_{IS}} + 0.0007}{1.4553} = \frac{0.0122 + 0.0007}{1.4553} = 0.0089$$

After that, the unknown amount of phenol in sample can be determined by multiplying  $M_P/M_{IS}$  with the mass of internal standard added to the mixture:

$$M_{P \text{ in sample}} = \frac{M_P}{M_{IS}} \times M_{IS} = 0.0089 \times 0.9288 = 0.0083\text{g}$$

To calculate the amount of phenol in the lower phase liquid, an estimation based on percentage of phenol contain in the sample is done:

$$M_{P \text{ in lower phase}} = \frac{M_{P \text{ in sample}}}{M_{\text{sample}}} \times M_{\text{lower phase}} = \frac{0.0083}{0.4483} \times 1.2239 = 0.0225\text{g}$$

The calculation is repeated in the upper phase; however, phenol peak is not detected in gas chromatogram data. Hence, it shows that phenol is being extracted by ionic liquid, Bmim SCN since there is no phenol left in hexane (upper) phase. Mass balance of the system is calculated, which is when 100% mass balance is obtained, it shows that the before and after mass of phenol in the system is equal. However, if it

exceeds 100%, it shows that the mass of phenol recovered exceed the true amount of phenol in the system, while if it is less than 100% there are some phenols are not recovered and loss maybe due to experimental errors. Mass balance for run 8 is calculated as:

$$\text{Mass Balance (\%)} = \frac{\text{Mass Recovered(g)}}{\text{True Mass(g)}} \times 100 = \frac{0.0225}{0.0149} \times 100 = 151\%$$

### 4.3 Analysis of Upper & Lower Phase after mixing Ionic Liquid (Bmim SCN) and Acetic acid-Hexane

Table 4.4 shows the mass of acetic acid, hexane and ionic liquid, Bmim SCN which are used in run 9, 10, 11 and 12; and also the measure mass of upper and lower phase after extraction:

Table 4.4: Mass of component Before & After Mixing

Run	Concentrat -ion (%)	Before Mixing			After Mixing	
		Mass AcOH (g)	Mass Hexane (g)	Mass IL (g)	Mass Upper (g)	Mass Lower (g)
9	0.52%	0.0056	1.0628	1.085	0.9745	1.1789
10	2.00%	0.0218	1.0687	0.9337	0.8955	1.1287
11	5.17%	0.0533	0.9778	0.9172	0.9	1.0483
12	10.27%	0.1029	0.8987	0.9166	0.3573	1.5609

The upper and lower phase is then analyzed using gas chromatograph and Table 4.5 shows the summary of the calculation of mass acetic acid, where  $M_s$  is mass of sample,  $M_{IS}$  is mass of propanol as the internal standard,  $T_{AcOH}$  is phenol retention time in gas chromatogram,  $A_{AcOH}$  is the area of phenol peak curve,  $A_{IS}$  is the area of internal standard and  $M_{AcOH}$  is the mass of phenol and  $M_{AcOHt}$  is total mass of phenol in upper/lower phase. All values of mass are in grams (g):

**Table 4.5: Summary of The Calculation of Mass Acetic Acid**

Run	M <sub>s</sub>	M <sub>IS</sub>	T <sub>AcOH</sub>	A <sub>AcOH</sub>	A <sub>IS</sub>
9 Upper	0.3056	0.2847	0.5903	-	-
9 Lower	0.3999	0.2454	0.6453	3.074	6869
10 Upper	0.3523	0.2827	0.635	-	-
10 Lower	0.3703	0.2556	0.6259	3.004	373995
11 Upper	0.2996	0.2767	0.5763	-	-
11 Lower	0.3513	0.3191	0.6704	3.461	512682
12 Upper	0.0637	0.1118	0.1755	-	-
12 Lower	0.3699	0.2707	0.6406	3.533	1012860

Run	A <sub>AcOH</sub> / A <sub>IS</sub>	M <sub>AcOH</sub> / M <sub>IS</sub>	M <sub>AcOH</sub>	M <sub>AcOH</sub> / M <sub>s</sub>	M <sub>AcOHt</sub>
9 Upper	-	-	-	-	-
9 Lower	0.0011	0.0060	0.0015	0.37%	0.0043
10 Upper	-	-	-	-	-
10 Lower	0.0139	0.0356	0.0091	2.46%	0.0277
11 Upper	-	-	-	-	-
11 Lower	0.0288	0.0701	0.0224	6.37%	0.0668
12 Upper	-	-	-	-	-
12 Lower	0.0391	0.0939	0.0254	6.87%	0.1072

The values obtained in Table 4.5 are based on gas chromatogram data and the calculation to obtain the amount of acetic acid is same as calculation shown in previous section.

#### 4.4 Extraction Result

Since the formation of immiscible liquid phases only occur for run 8, 9, 10, 11 and 12, gas chromatography analysis is only done on those runs, since it is not necessary to determine the amount of component in bio-oil when phase separation doesn't occur. Table 4.6 shows the result of the extraction process, based on gas chromatograms data obtained. Mass balance is also calculated and there is slight difference in the mass balance, probably due to inaccurate mass measurement after separation took place. Table 4.6 shows that all components are being extracted by ionic liquid since there are no phenol or acetic acid being detected by the gas chromatography in the hexane (upper) phase of the immiscible liquids, as shown in Table 4.6 below:

Table 4.6: Result of Extraction Process for Run 8, 9, 10, 11 and 12

Run	Component in Hexane	Before Extraction	After Extraction		Mass Balance (%)
		Mass of Component in Hexane(g)	Mass of Component in Hexane (Upper) Phase (g)	Mass of Component in IL (Lower) Phase (g)	
8	Phenol	0.0149	0	0.0225	151.01
9	Acetic Acid	0.0056	0	0.0043	76.79
10	Acetic Acid	0.0218	0	0.0277	127.06
11	Acetic Acid	0.0533	0	0.0668	125.33
12	Acetic Acid	0.1029	0	0.1072	104.18

Following that, the result of extraction process is plotted using bar chart. For run 8, Figure 4.3 shows the amount of phenol before and after the extraction process in both upper and lower phase:

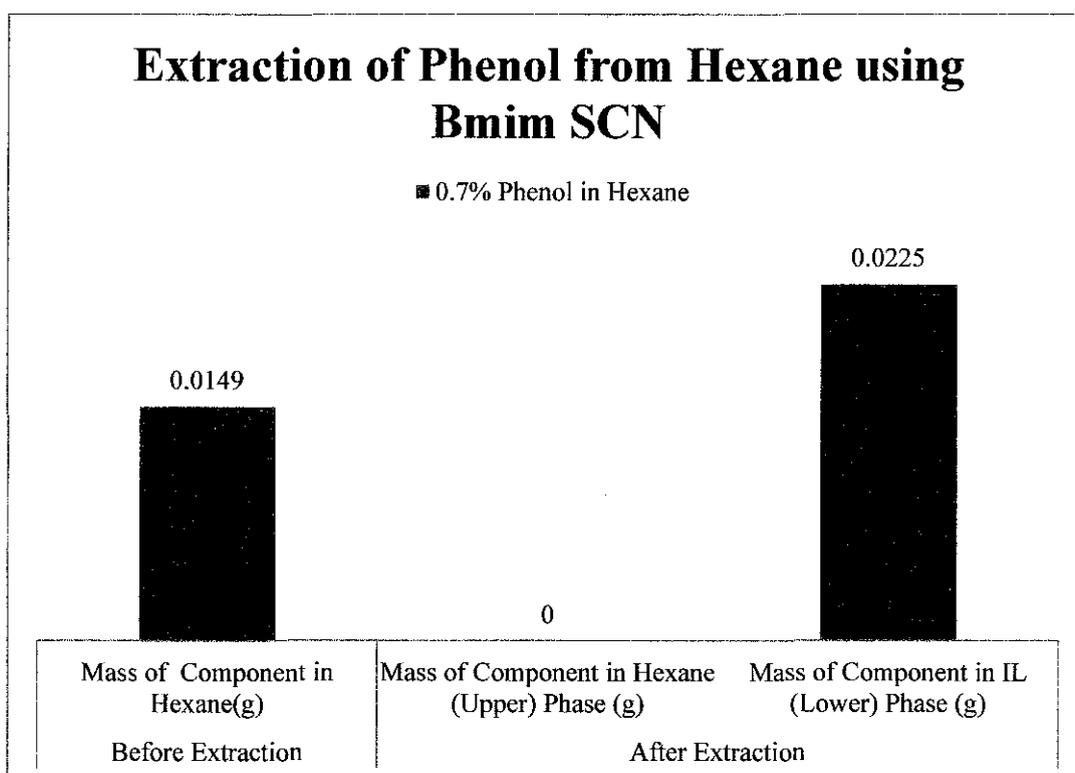


Figure 4.3: Extraction of Phenol from Hexane using Bmim SCN

For run 9, 10, 11 and 12, Figure 4.4, 4.5, 4.6 and 4.7 shows the amount of acetic acid before and after the extraction process in both upper and lower phase, respectively:

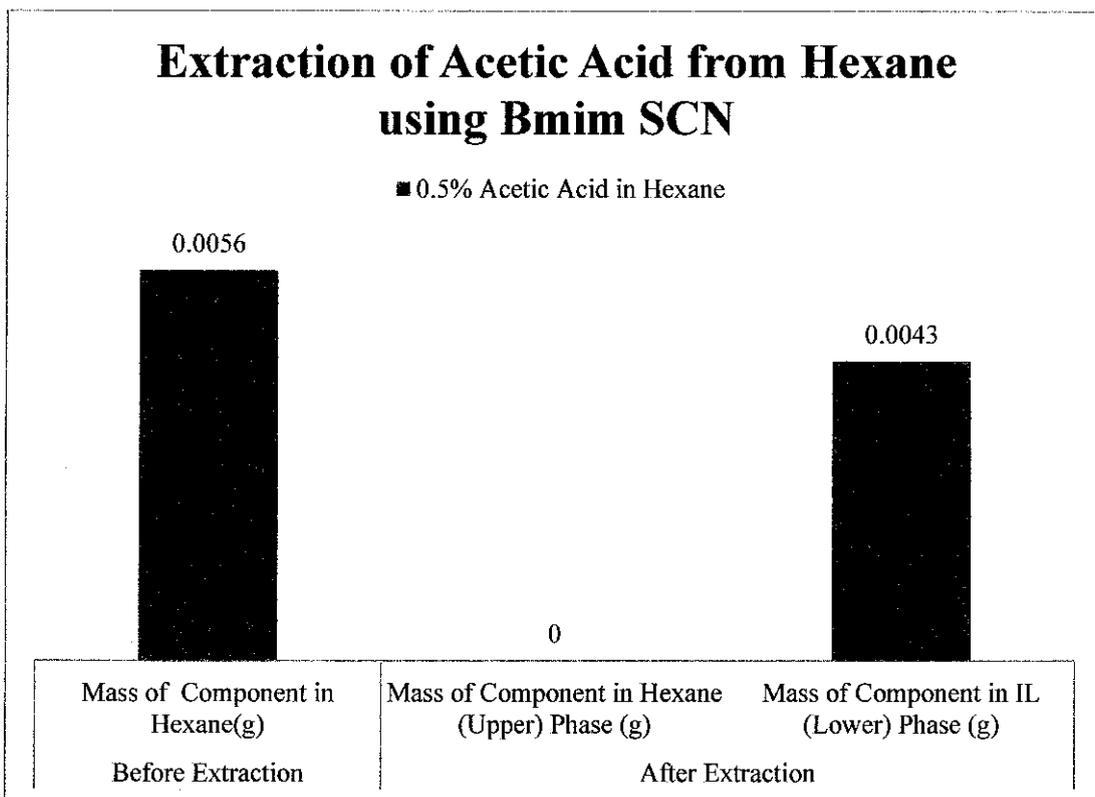


Figure 4.4: Extraction of Acetic Acid from Hexane using Bmim SCN (0.5% Acetic Acid in Hexane)

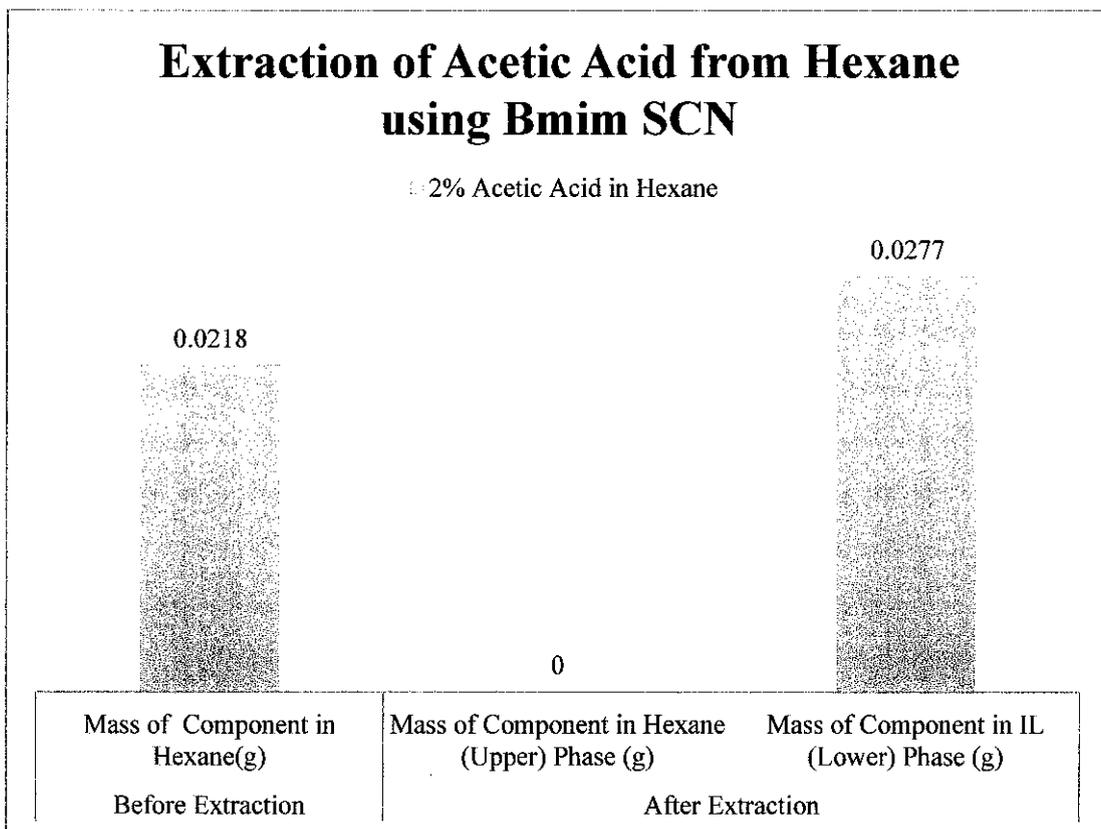


Figure 4.5: Extraction of Acetic Acid from Hexane using Bmim SCN (2% Acetic Acid in Hexane)

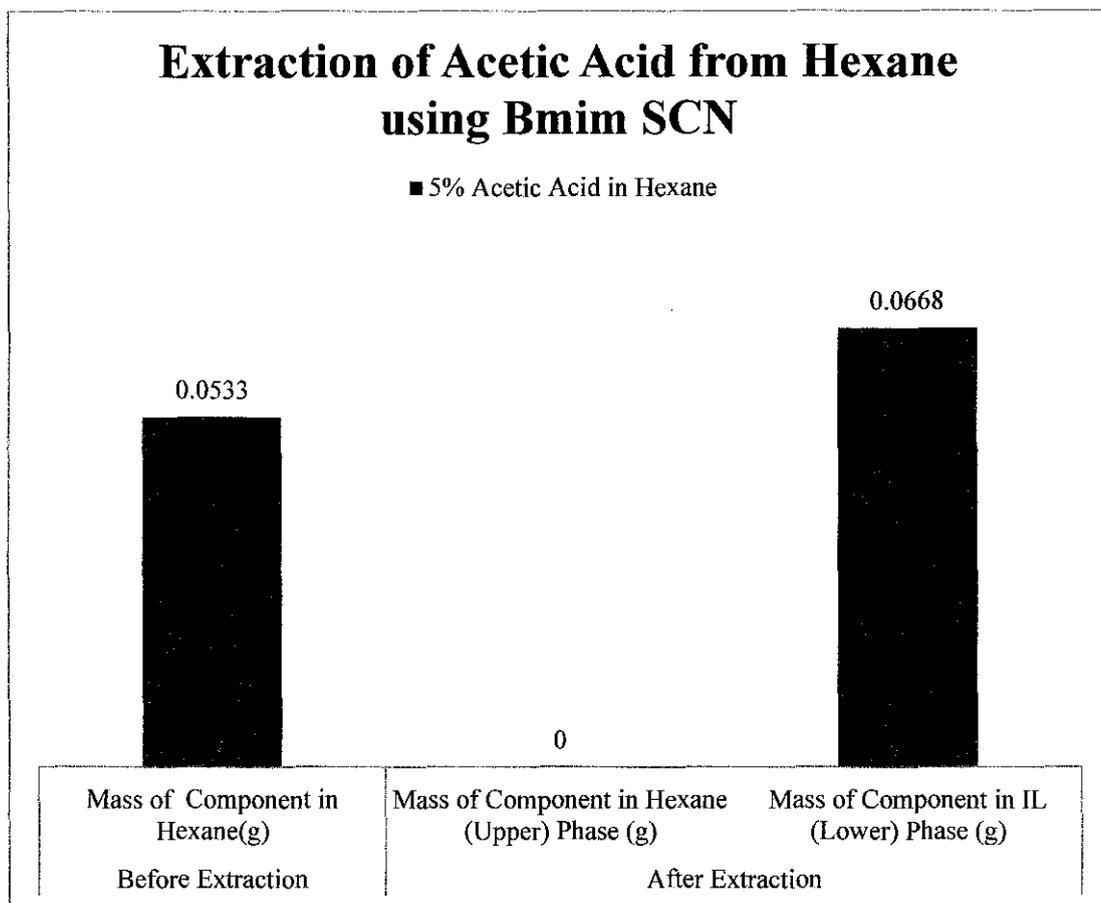


Figure 4.6: Extraction of Acetic Acid from Hexane using Bmim SCN (5% Acetic Acid in Hexane)

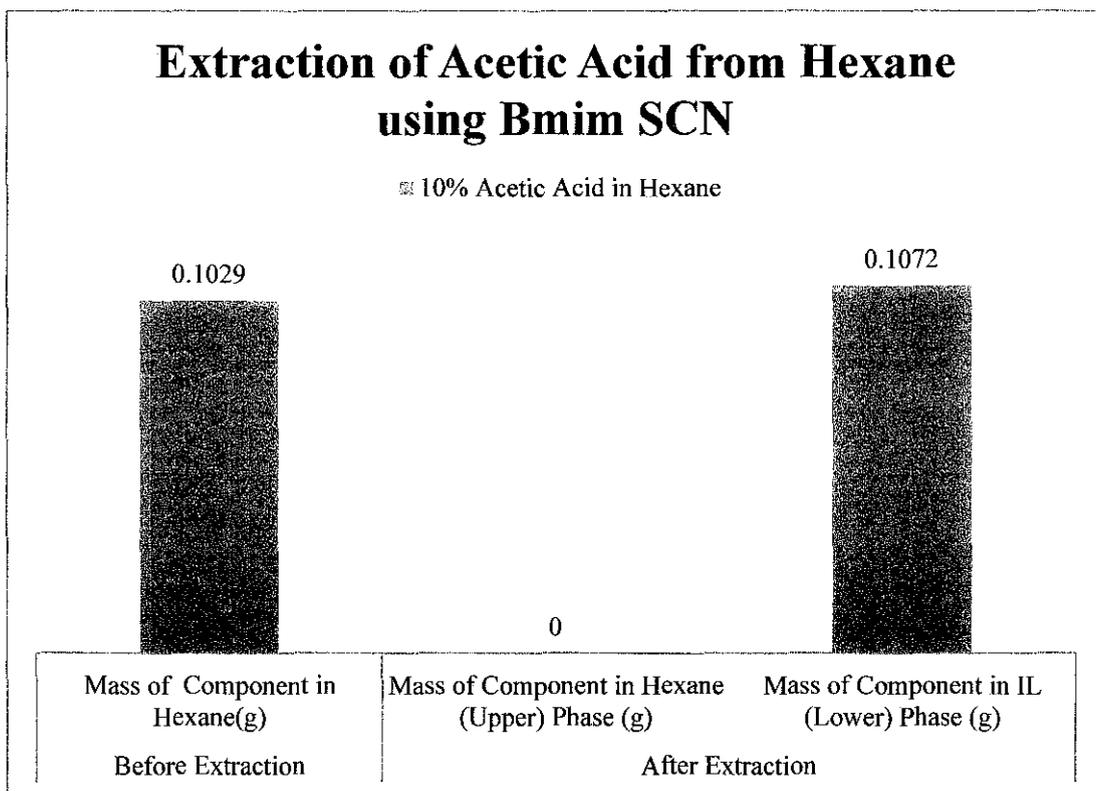


Figure 4.7: Extraction of Acetic Acid from Hexane using Bmim SCN (10% Acetic Acid in Hexane)

#### 4.5 Discussion

The ionic liquids Bmim SCN and Bmim OTf were tested to have good miscibility with bio-oil K4K6 and K2, even dried K4K6. This leads to an inappropriate combination for separation, because of their inability to produce two liquid phases. Bio-oil does consist of hydrophilic and hydrophobic components, and may be able to be separated using ionic liquid. Hence, we moved out to test by creating emulated bio-oil (EBO).

Three types of EBO were made: 1) by mixing the main components (phenol, acetic acid, furfural and p-cresol) of bio-oil 2) by mixing hexane and phenol and 2) by mixing hexane and acetic acid.

The first mixture of EBO still didn't produce phase separation, due to its good miscibility with ionic liquid. After mixing the second and third mixtures of EBO with ionic liquid, two liquid phases were observed. Using this combination, we were able to measure how much phenol and acetic acid can be extracted by ionic liquid.

Gas chromatograph results showed that the components of bio-oil which are phenol and acetic acid were being completely extracted by ionic liquid, since the component was not detected in the hexane phase.

#### 4.6 Water Content Analysis

Two types of bio-oil are used in order to determine its water content, which are K4K6 and K2. The samples are tested using Karl Fischer titrator with volumetric titration method. Figure 4.8 below shows one of the readings taken for testing K4K6:

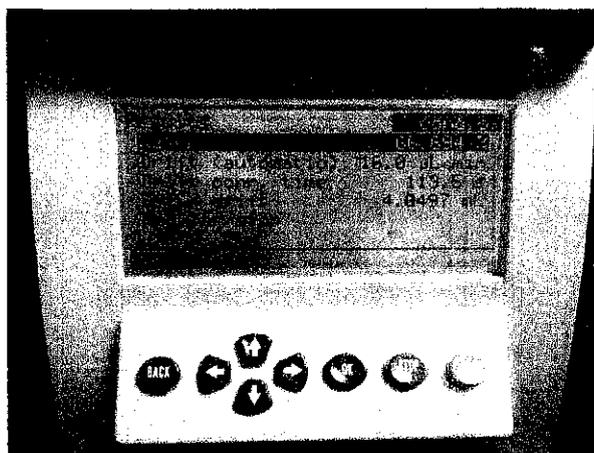


Figure 4.8: One of the Readings Taken for Testing K4K6

Table 4.7 below shows the result for the test:

**Table 4.7: Water Content Analysis Result for K4K6 and K2**

<b>Bio-oil</b>	<b>Water content (%)</b>
K4K6	66.95
K2	0.18

## **CHAPTER 5 : CONCLUSION & RECOMMENDATION**

To conclude, in order to study the acid separation from bio-oil using ionic liquid, appropriate techniques and measures needed to be taken. To measure acid reduction after extraction process, Chromatography analysis was done.

Based on the results obtained and early observations, two types of ionic liquid, Bmim SCN and Bmim OTF are able to extract acetic acid and phenol in from a simulated bio-oil. However, the real bio-oil and ionic liquid has good miscibility with each other, hence it is quite an inappropriate combination for acid separation.

Further studies on creating a new different kind of ionic liquid should be done in order to specifically extract only organic acids from bio-oil without taking out its main components.

Regarding bio-oil upgrading, acid separation from bio-oil using ionic liquid should be done commercially if it is proven to be effective not only process-wise but also economic-wise. It is mainly because to reduce our dependant on fossil fuel as our only source of energy.

## WORKS CITED

- Demirbas, A. (2011). Competitive liquid biofuel from biomass. *Applied Energy* 88, 17-28.
- Kim, S.-J., Jung, S.-H., & Kim, J.-S. (2010). Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresource Technology* 101, 9294–9300.
- Mart'ak, J., & Schlosser, S. (2007). Extraction of lactic acid by phosphonium ionic liquids. *Separation and Purification Technology* 57, 483–494.
- Matsumoto, M., Kochiduki, K., Fukunishi, K., & Kondo, K. (2007). Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *Lactobacillus rhamnosus*. *Separation and Purification Technology* 40, 97–101.
- Oliveira, E. L., Grande, C. A., & Rodrigues, A. E. (2009). Steam Methane Reforming in a Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst: Kinetics and Diffusional Limitations in Extrudates. *THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING*, 87, 945-956.
- Pimenidou, P., & Dupont, V. (2012). Characterisation of palm empty fruit bunch (PEFB) and pinewood bio-oils and kinetics of their thermal degradation. *Bioresource Technology*, 1-8.
- Sukhbaatar, B., Steele, P. H., Ingram, L. L., & Kim, M. G. (2009). An Exploratory Study on The Removal of Acetic Acid and Formic Acids from Bio-oil. *Bi-Resource*, 4(4), 1319-1329.

## **APPENDICES**

### **APPENDIX A: Phenol-Propanol Calibration Curve Gas Chromatogram Data**

**APPENDIX A-1: 0.13% Phenol in Propanol**

**APPENDIX A-2: 0.24% Phenol in Propanol**

**APPENDIX A-3: 0.69% Phenol in Propanol**

**APPENDIX A-4: 0.77% Phenol in Propanol**

**APPENDIX A-5: 1.68% Phenol in Propanol**

### **APPENDIX B: Acetic Acid-Propanol Calibration Curve Gas Chromatogram Data**

**APPENDIX B-1: 0.45% Phenol in Propanol**

**APPENDIX B-2: 2.85% Phenol in Propanol**

**APPENDIX B-3: 5.53% Phenol in Propanol**

**APPENDIX B-4: 13.14% Phenol in Propanol**

### **APPENDIX C: Gas Chromatogram Data for Analysis of Upper & Lower Phase after mixing Ionic Liquid (Bmim SCN) and Phenol-Hexane**

**APPENDIX C-1: Run 8 Upper Liquid Phase**

**APPENDIX C-2: Run 8 Lower Liquid Phase**

### **APPENDIX D: Gas Chromatogram Data for Analysis of Upper & Lower Phase after mixing Ionic Liquid (Bmim SCN) and Acetic acid-Hexane**

**APPENDIX D-1: Run 9 Upper Liquid Phase**

**APPENDIX D-2: Run 9 Lower Liquid Phase**

**APPENDIX D-3: Run 10 Upper Liquid Phase**

**APPENDIX D-4: Run 10 Lower Liquid Phase**

**APPENDIX D-5: Run 11 Upper Liquid Phase**

**APPENDIX D-6: Run 11 Lower Liquid Phase**

**APPENDIX D-7: Run 12 Upper Liquid Phase**

**APPENDIX D-8: Run 12 Lower Liquid Phase**

**APPENDIX E: Gas Chromatogram Data for Pure Components**

**APPENDIX E-1: Propanol**

**APPENDIX E-2: Hexane**

**APPENDIX E-3: Acetic Acid**

**APPENDIX F: Gas Chromatogram for Mixture**

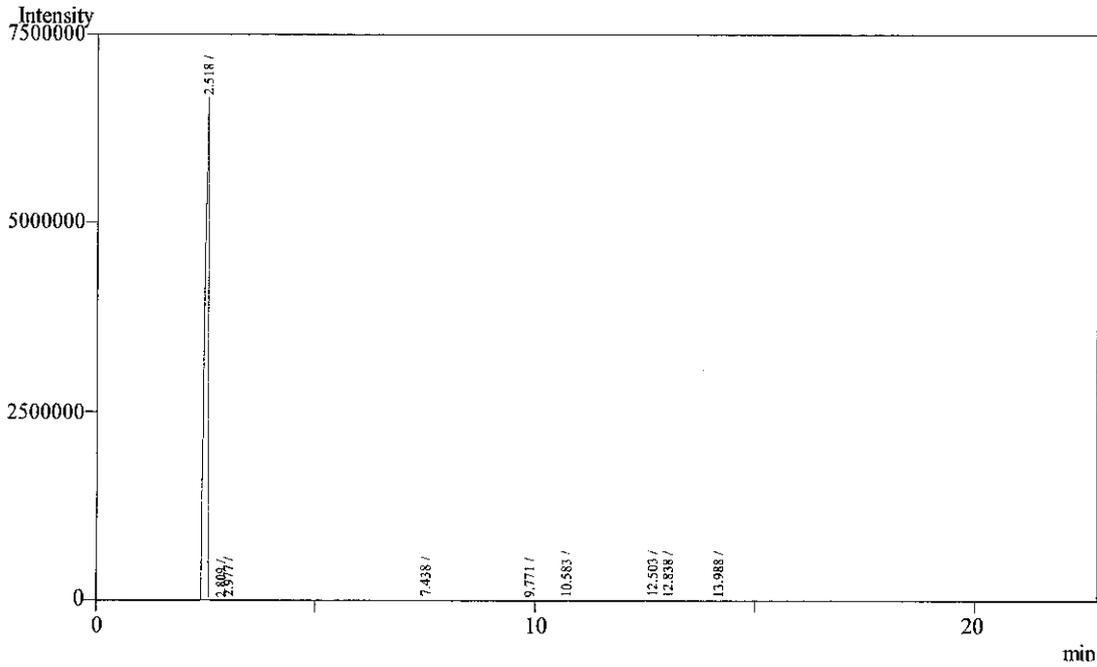
**APPENDIX F-1: Phenol-Hexane**

**APPENDIX F-2: Acetic Acid-Hexane**

APPENDIX A-1

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 User Name : Admin  
 Vial# : 1  
 Sample Name : 0.13a  
 Sample ID : 0.13a  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\0.13a.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 0.13a  
 0.4ul

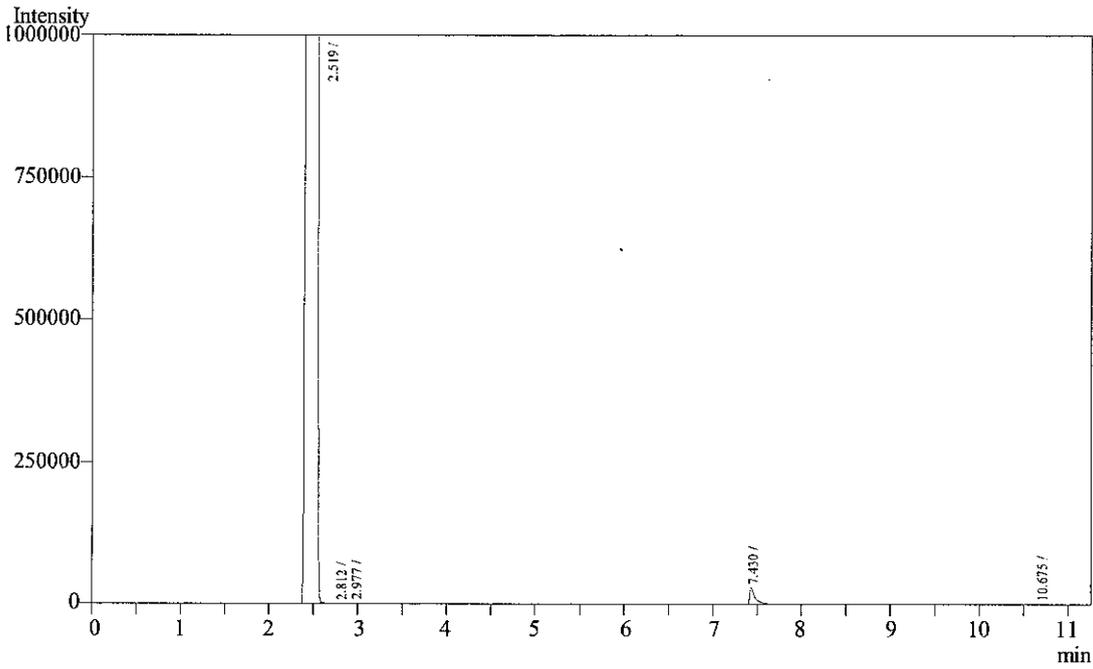


Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Compd Name
1	2.518	39559416	6612925	0.000			
2	2.809	1450	932	0.000			
3	2.977	1525	991	0.000			
4	7.438	61211	14263	0.000			
5	9.771	6669	1384	0.000			
6	10.583	21922	2125	0.000			
7	12.503	17118	6196	0.000			
8	12.838	1855	833	0.000			
9	13.988	1369	678	0.000			
Total		39672535	664032				

APPENDIX A-2

Analysis Date & Time : 7/13/2012 11:46:06 AM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : 0.24a  
 Sample ID : 0.24a  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\0.24a.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 0.24a  
 0.4ul



Peak#	Ret. Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.519	40155650	6607717	0.000			
2	2.812	1422	899	0.000			
3	2.977	226	211	0.000			
4	7.430	123626	29786	0.000			
5	10.675	3878	1106	0.000			
Total		40284802	6639719				

APPENDIX A-3

Analysis Date & Time : 7/12/2012 6:21:55 PM  
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 Sample ID : 0.69a  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

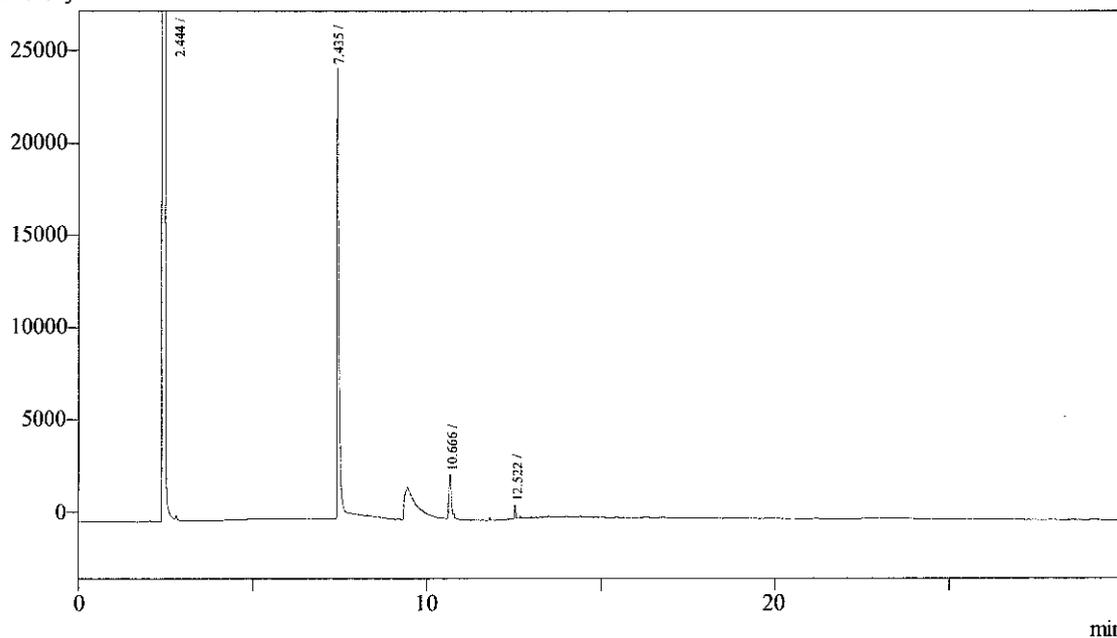
Data Name : C:\GCsolution\Data\hafizah\120712\0.69.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm

[Description]

0.69a

0.4ul

Intensity

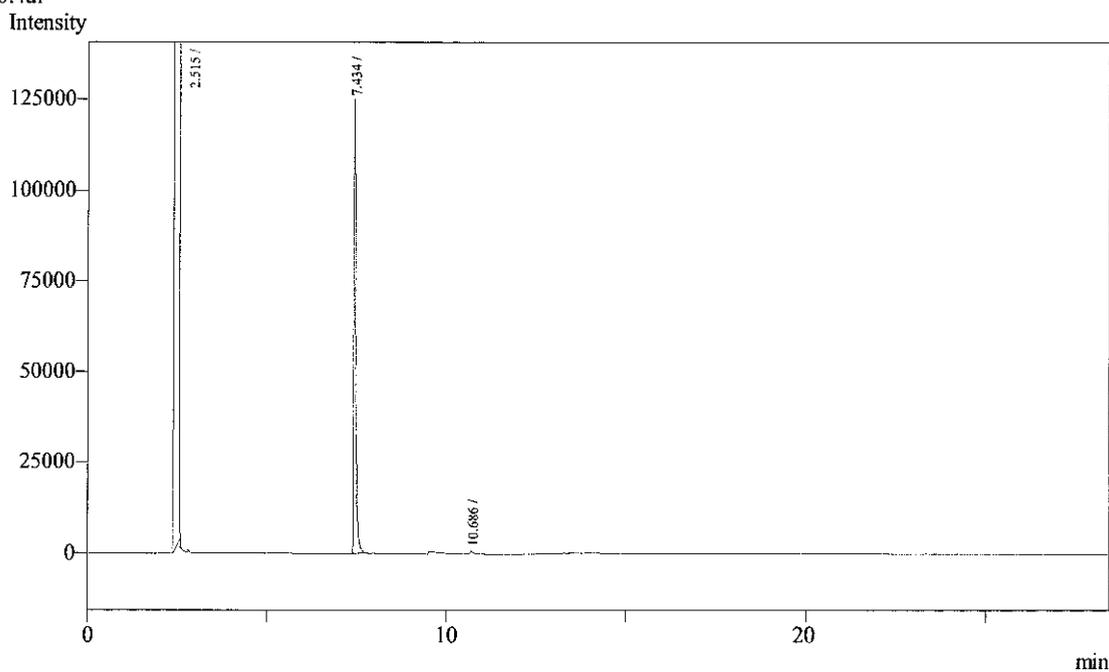


Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.444	10002359	3693171	0.000			
2	7.435	77592	23987	0.000			
3	10.666	9558	2271	0.000			
4	12.522	1541	729	0.000			
Total		10091050	3720158				

APPENDIX A-4

Analysis Date & Time : 7/12/2012 4:43:29 PM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : 0.77a  
 Sample ID : 0.77a  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\0.77a.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 0.77a  
 0.4ul



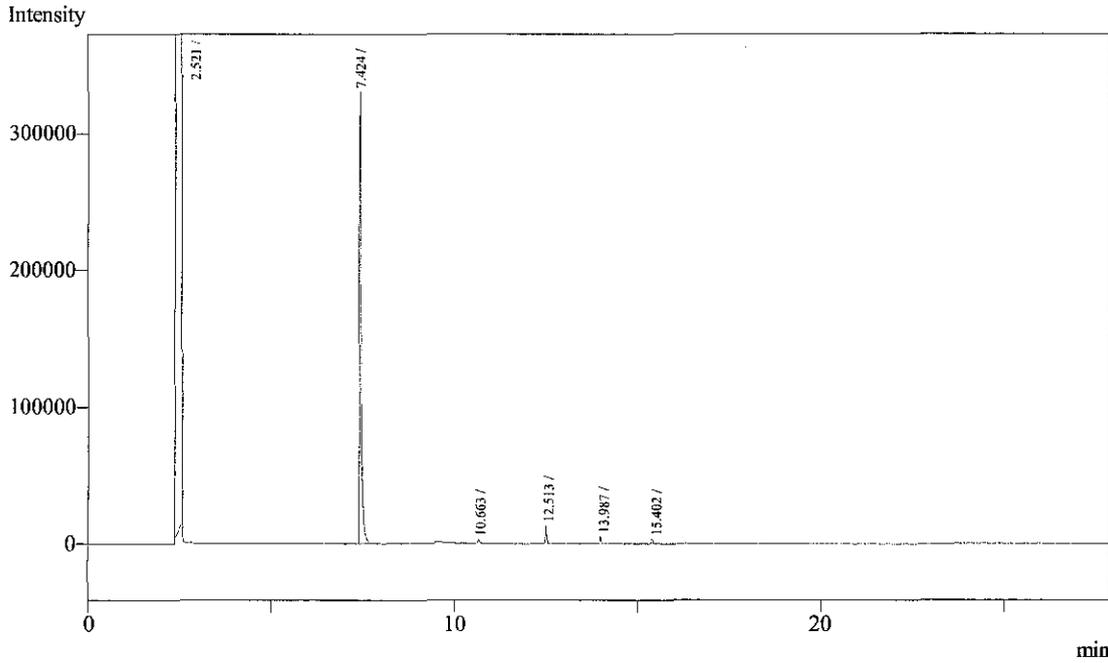
Peak#	Ret. Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.515	36230429	6379062	0.000			
2	7.434	404856	123621	0.000			
3	10.686	5145	1027	0.000			
Total		36640430	6503710				

APPENDIX A-5

Analysis Date & Time : 7/13/2012 10:56:06 AM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : 1.68  
 Sample ID : 1.68  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\1.68.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm

[Description]  
 1.68  
 0.4ul

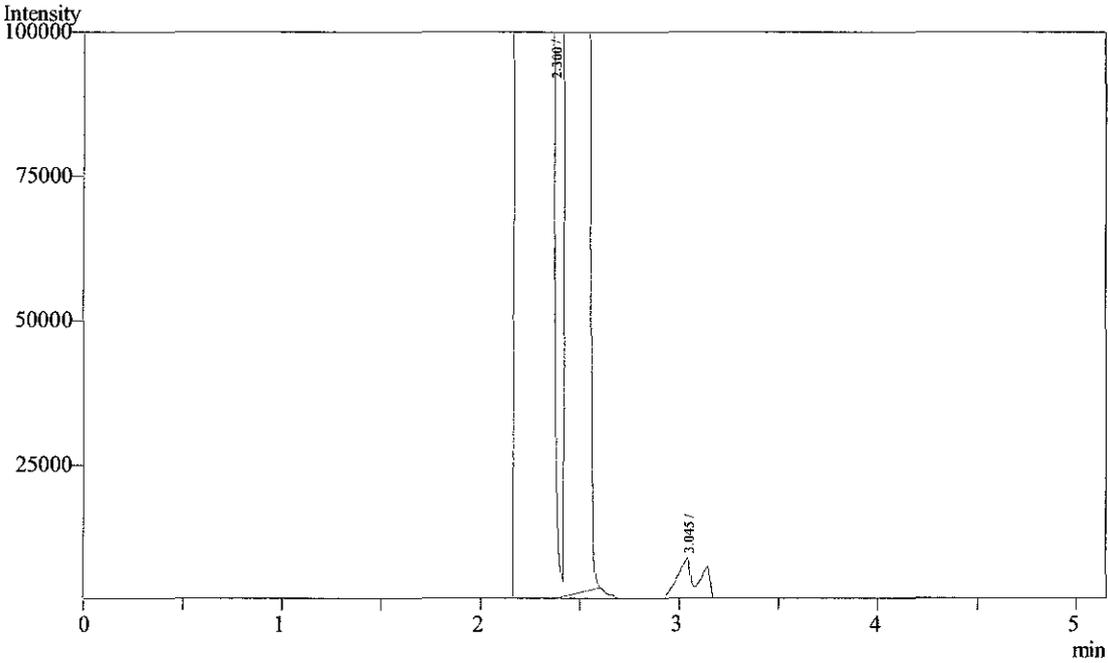


Peak#	Ret. Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.521	42719465	6817931	0.000			
2	7.424	1048138	328233	0.000			
3	10.663	10088	2981	0.000			
4	12.513	29591	13019	0.000			
5	13.987	10499	5327	0.000			
6	15.402	9869	3577	0.000			
Total		43827650	7171068				

APPENDIX B-1

Analysis Date & Time : 7/24/2012 3:18:14 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : AA 0.4  
 Sample ID : AA 0.4  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\AA 0.4.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 AA 0.4  
 0.4ul

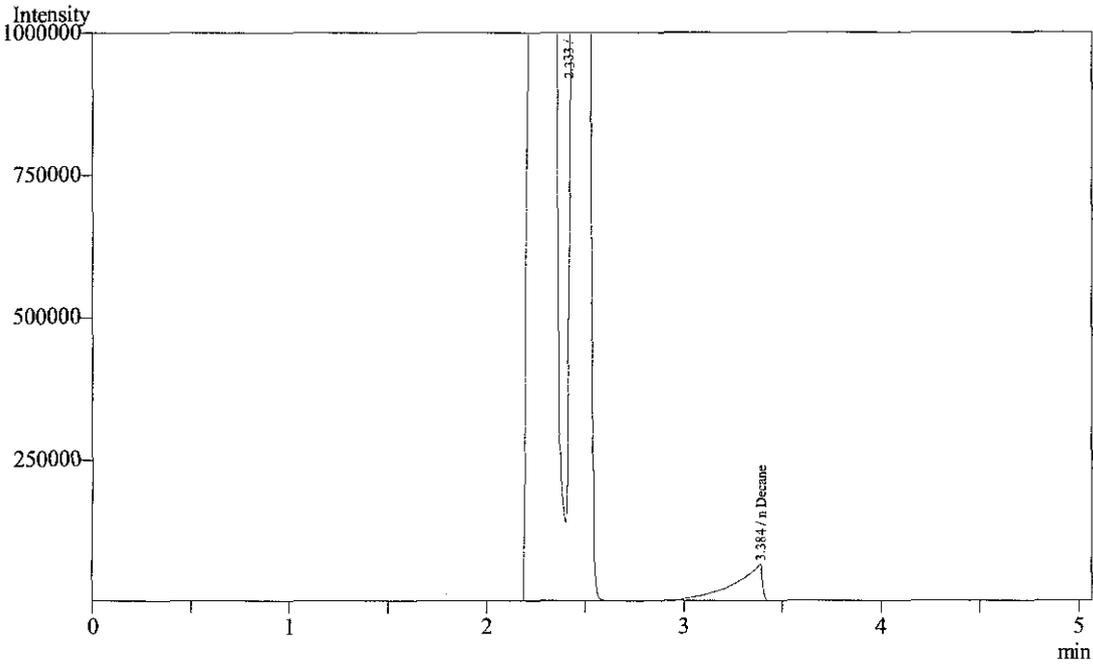


Peak#	Ret. Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.300	61237605	5572298	0.000			
2	3.045	60880	7629	0.000			
Total		61298485	5579927				

APPENDIX B-2

Analysis Date & Time : 7/24/2012 3:32:58 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : AA 2.8  
 Sample ID : AA 2.8  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

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 AA 2.8  
 0.4ul

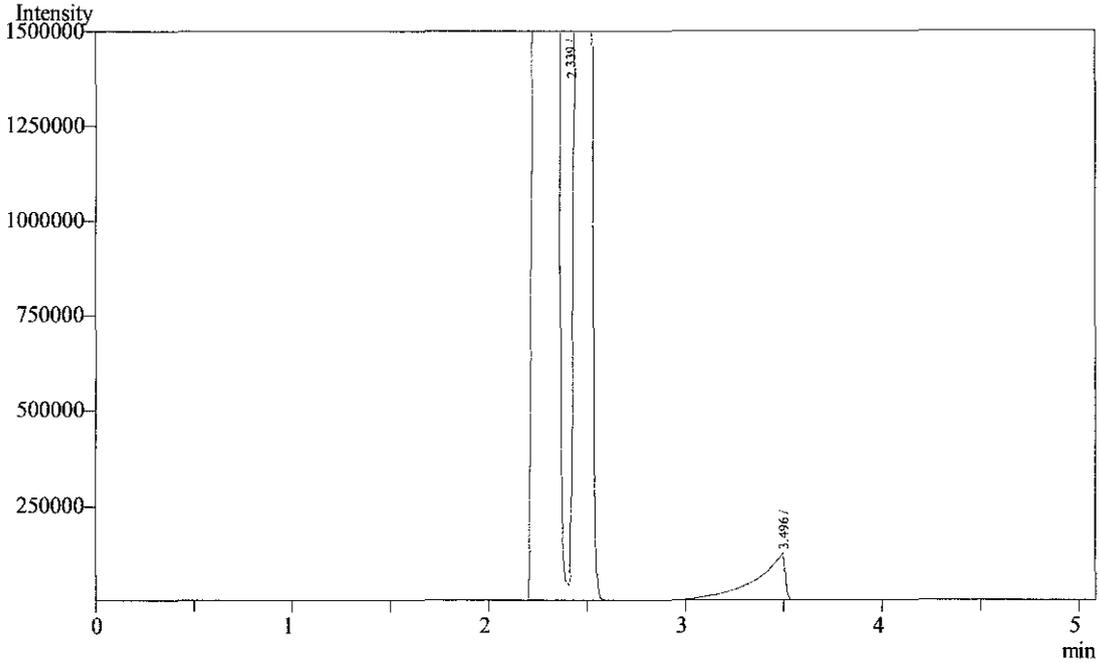


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.333	59755710	5777337	0.000				
2	3.384	653500	65457	0.000	ug/m			n Decane
Total		60409210	5842794					

APPENDIX B-3

Analysis Date & Time : 7/24/2012 3:46:51 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : AA 5.5  
 Sample ID : AA 5.5  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [I]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\AA 5.5.gcd  
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 AA 5.5  
 0.4ul

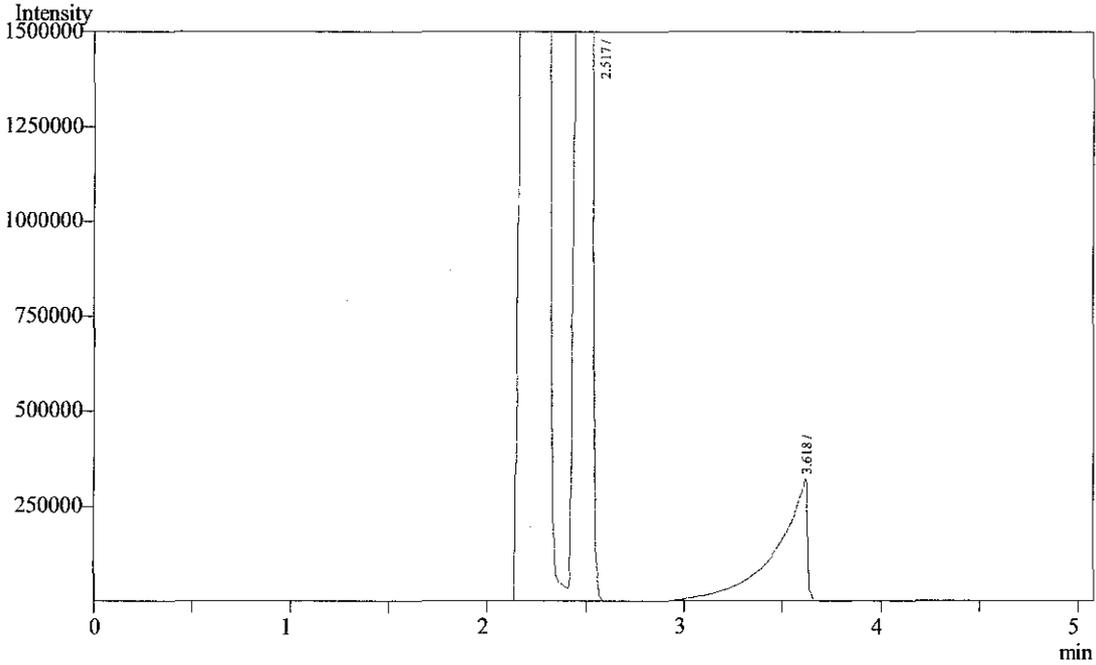


Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.339	56284187	5586131	0.000			
2	3.496	1315947	123769	0.000			
Total		57600134	5709900				

APPENDIX B-4

Analysis Date & Time : 7/24/2012 4:01:03 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : AA 13  
 Sample ID : AA 13  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\AA 13.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 AA 13  
 0.4ul

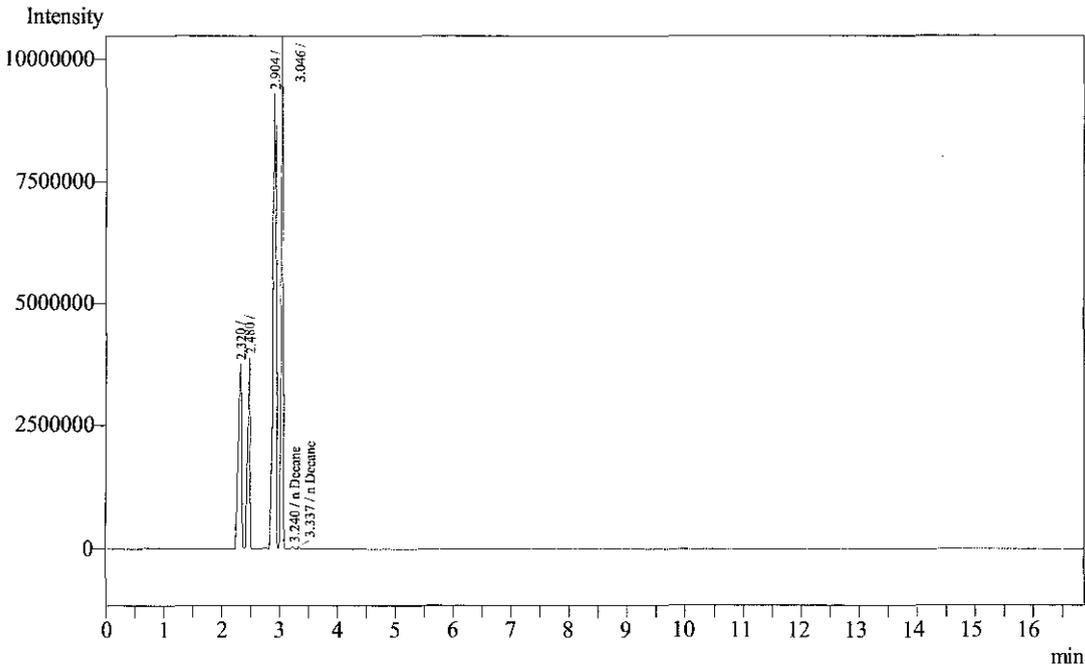


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.517	54650483	5209317	0.000				
2	3.618	3504956	317836	0.000		S		
Total		58155439	5527153					

APPENDIX C-1

Analysis Date & Time : 8/8/2012 11:03:21 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : TOP phenol hexane  
 Sample ID : TOP phenol hexane  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\Putri\TOP phenol hexane.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 TOP phenol hexane  
 0.4ul

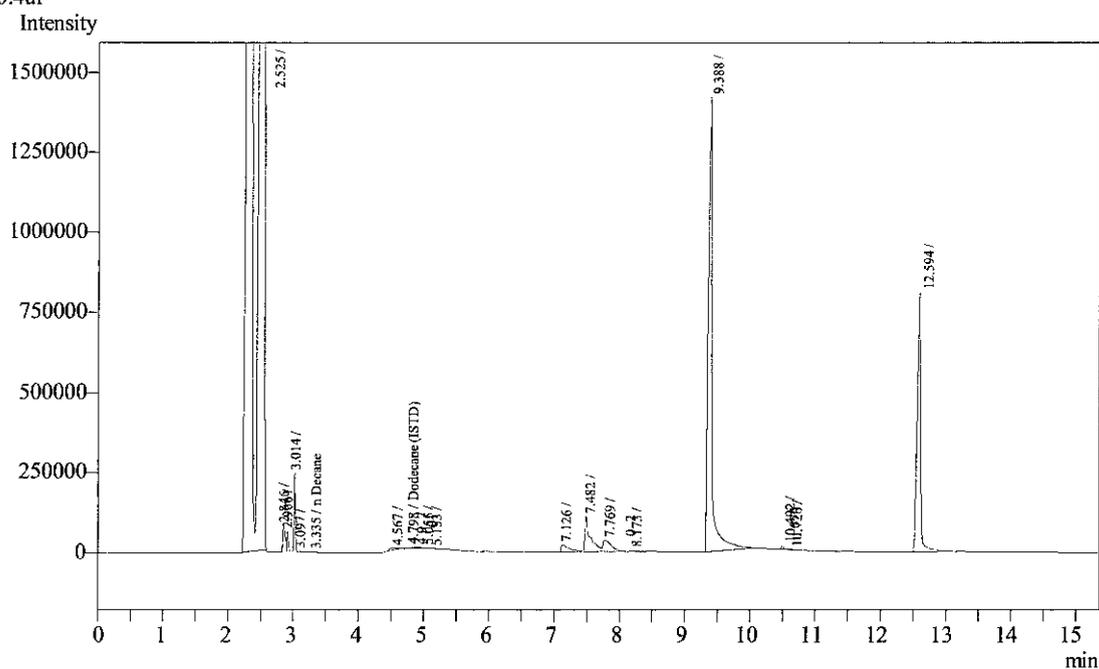


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.320	15944997	3697192	0.000				
2	2.480	10184882	3857616	0.000				
3	2.904	35983638	9192302	0.000				
4	3.046	21670752	10628308	0.000		V		
5	3.240	136611	50867	0.000	ug/m		1	n Decane
6	3.337	84068	57150	0.000	ug/m		1	n Decane
Total		84004948	27483435					

APPENDIX C-2

Analysis Date & Time : 8/8/2012 11:36:16 AM  
 User Name : Admin  
 Vial# : 0  
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 Sample ID : BOT phenol hexane  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\Putri\BOT phenol hexane.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 BOT phenol hexane  
 0.4ul

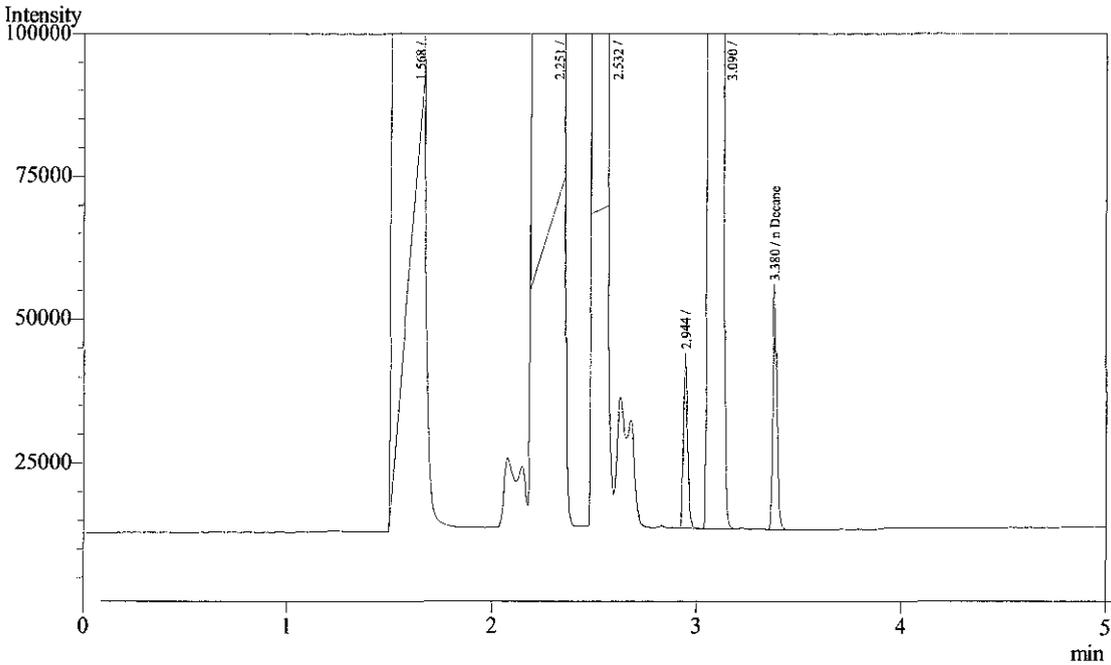


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Compd Name
1	2.525	52327333	5618261	0.000				
2	2.846	222205	83476	0.000				
3	2.906	111428	65112	0.000		V		
4	3.014	346552	243445	0.000		V		
5	3.097	8052	3533	0.000		V		
6	3.335	1802	1238	0.060	ug/m		1	n Decane
7	4.567	58105	4219	0.000				
8	4.798	34347	3436	0.000	ug/m		2	Dodecane (ISTD)
9	4.957	13352	2535	0.000		V		
10	5.055	3325	1652	0.000		V		
11	5.101	4086	1422	0.000		V		
12	5.153	3802	1037	0.000		V		
13	7.126	224082	22772	0.000				
14	7.482	640244	108157	0.000		V		
15	7.769	335662	37092	0.000		V		
16	8.072	8734	2384	0.000		V		
17	8.173	7537	3057	0.000		V		
18	9.388	5853864	1413202	0.000				
19	10.492	23094	10693	0.000				
20	10.674	1509	683	0.000				
21	10.720	1962	1056	0.000		V		
22	12.594	2996833	800809	0.000		S		

APPENDIX D-1

Analysis Date & Time : 7/24/2012 9:35:39 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS9 top  
 Sample ID : PS9 top  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS9 top.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 PS9 top  
 0.4ul



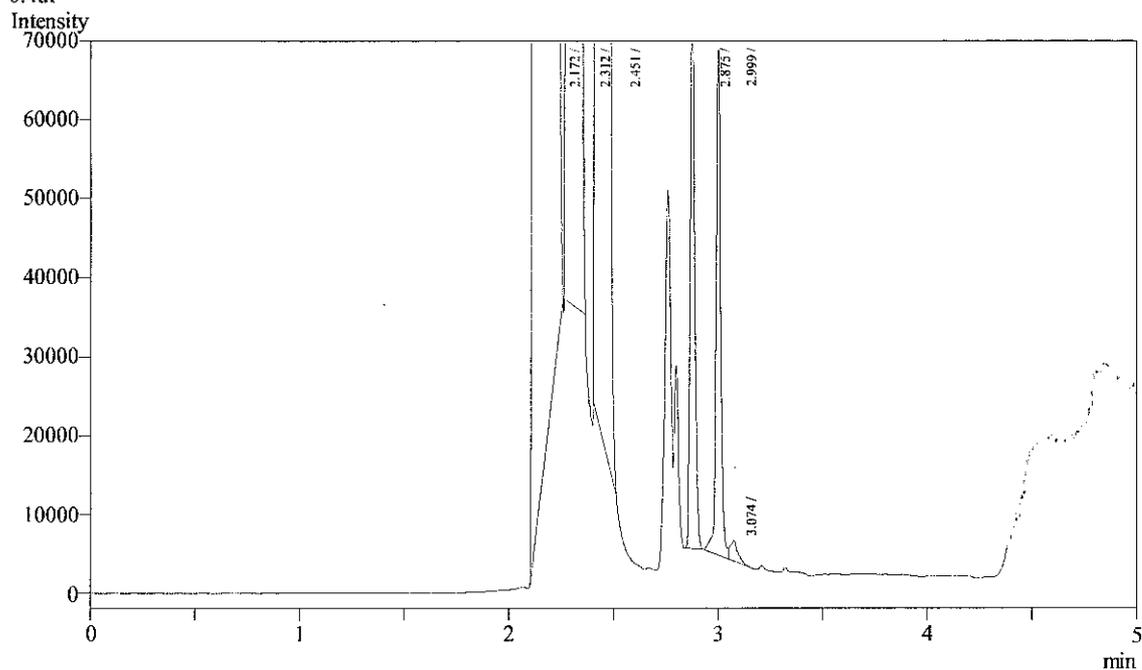
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.568	13059875	2539375	0.000				
2	2.251	26992563	5465090	0.000				
3	2.532	7687705	3381332	0.000				
4	2.944	42780	30219	0.000				
5	3.090	16147211	8604538	0.000				
6	3.380	60549	41310	0.000	ug/m			I n Decane
7	12.524	6507	2520	0.000				
Total		63997190	20064384					

APPENDIX D-2

Analysis Date & Time : 7/24/2012 12:30:10 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS9 bot  
 Sample ID : PS9 bot  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS9 bot.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm

[Description]  
 PS9 bot  
 0.4ul

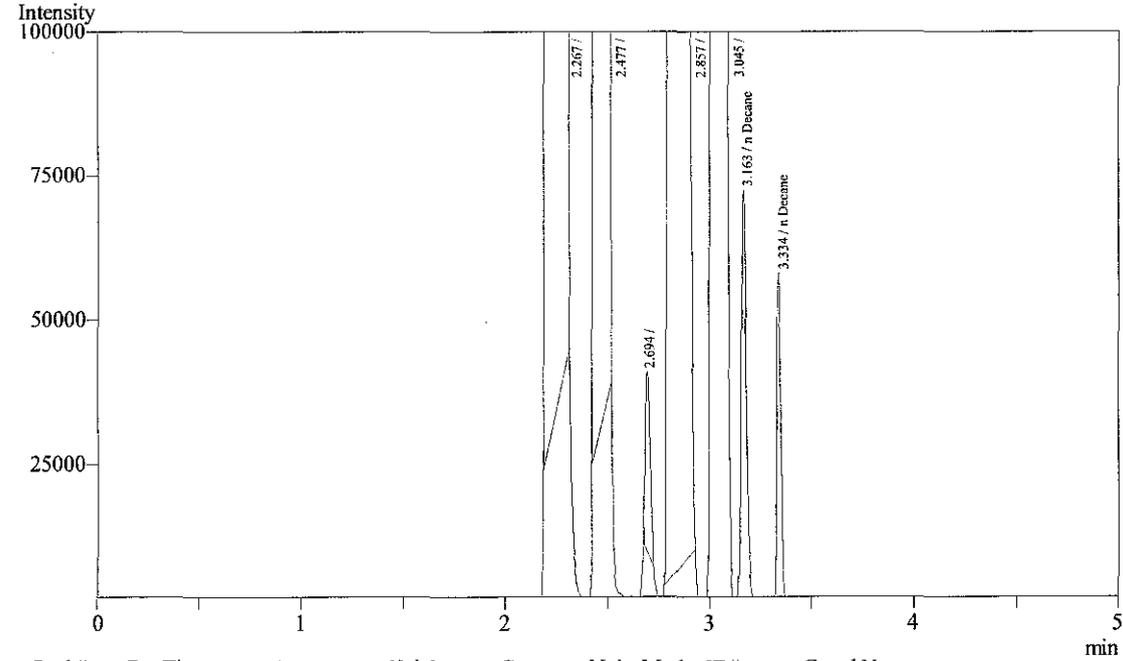


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.172	9899385	2821030	0.000				
2	2.312	6401159	2979345	0.000				
3	2.451	6296876	2890511	0.000				
4	2.875	95591	66000	0.000				
5	2.999	93034	63082	0.000				
6	3.074	6869	2604	0.000		V		
7	7.038	160770	43238	0.000				
8	7.088	349429	41038	0.000		V		
9	7.492	489467	73263	0.000		V		
10	7.616	476970	58454	0.000		V		
11	7.961	32589	5984	0.000		V		
12	8.055	14365	3830	0.000		V		
13	8.163	15914	6684	0.000		V		
14	8.898	12004	2306	0.000				
15	9.409	12181462	2070151	0.000		S		
16	10.253	2169	531	0.000		T		
17	10.412	1079	254	0.000		TV		
18	10.488	122825	61369	0.000		T		
19	10.708	2726	1646	0.000		TV		
20	10.969	2972	1229	0.000		T		
21	11.121	2521	722	0.000		T		
22	12.643	7681885	1410449	0.000		S		

APPENDIX D-3

Analysis Date & Time : 7/24/2012 10:18:13 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS10 top  
 Sample ID : PS10 top  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS10 top.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 PS10 top  
 0.4ul



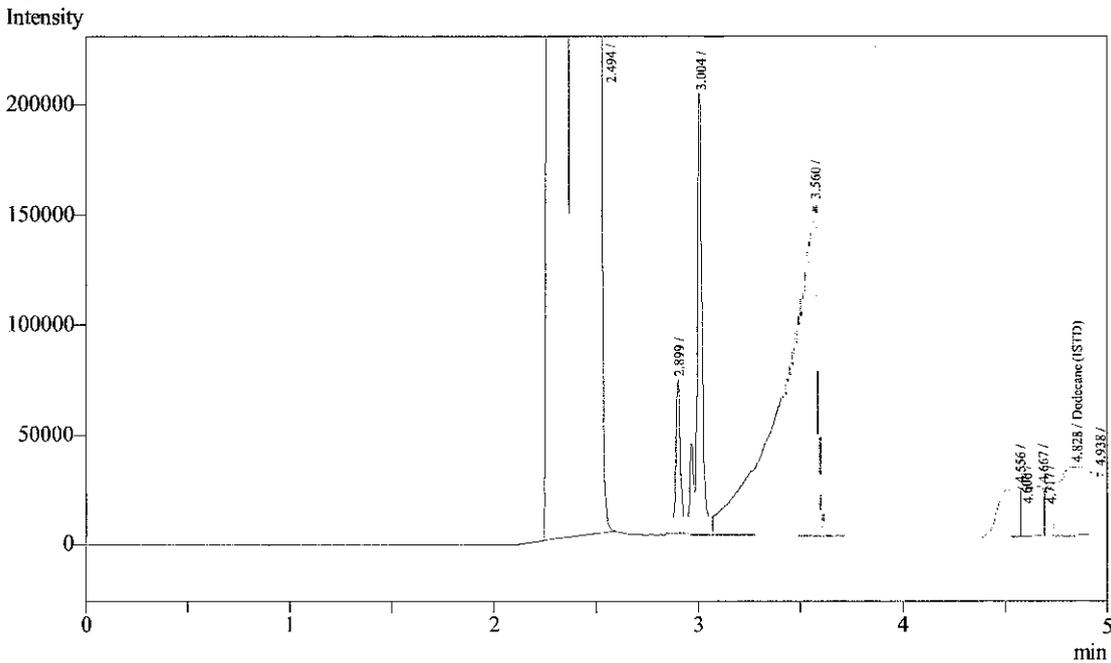
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.267	13648477	4052745	0.000				
2	2.477	9095101	3632579	0.000				
3	2.694	52493	30985	0.000				
4	2.857	33085679	12515366	0.000				
5	3.045	21939347	10762197	0.000				
6	3.163	126418	71473	0.000	ug/m	V		1 n Decane
7	3.334	83664	57030	0.000	ug/m			1 n Decane
8	12.533	1027	463	0.000				
9	13.138	1439	784	0.000				
Total		78033645	31123622					

APPENDIX D-4

Analysis Date & Time : 7/24/2012 1:02:01 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS10 bot  
 Sample ID : PS10 bot  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS10 bot.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm

[Description]  
 PS10 bot  
 0.4ul



Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	I #	Compd Name
1	2.494	26952239	4737745	0.000				
2	2.899	121125	68610	0.000				
3	3.004	373995	198383	0.000		V		
4	3.560	1697380	151169	0.000		V		
5	4.556	161065	22683	0.000				
6	4.606	81458	22756	0.000		V		
7	4.667	74379	22617	0.000		V		
8	4.717	60937	22260	0.000		V		
9	4.828	303483	31383	0.000	ug/m	V	2	Dodecane (ISTD)
10	4.938	169321	29384	0.000		V		
11	5.036	229883	25997	0.000		V		
12	5.199	58144	21299	0.000		V		
13	5.258	430996	20479	0.000		V		
14	7.032	649594	52171	0.000				
15	7.504	646549	100104	0.000		V		
16	7.614	437987	60605	0.000		V		
17	7.953	48857	7981	0.000		V		
18	8.059	27779	6141	0.000		V		
19	8.167	54858	10042	0.000		V		
20	8.503	4423	768	0.000		V		
21	9.128	1246	509	0.000		V		
22	9.180	3436	1673	0.000		V		

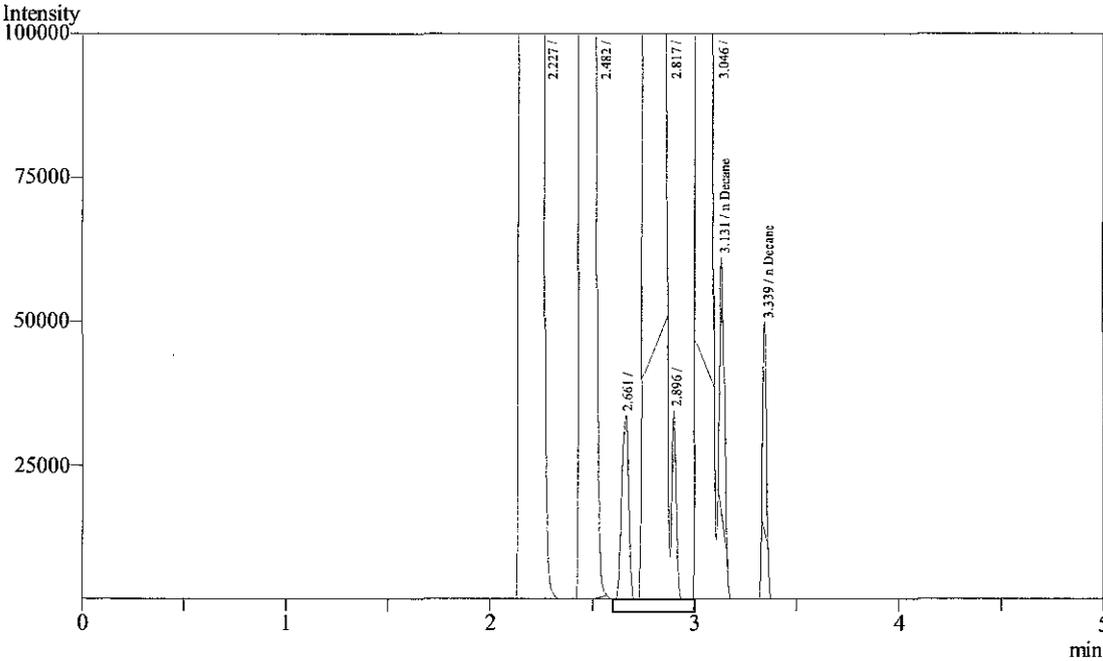
## APPENDIX D-4

23	9.414	13087942	2157028	0.000	SV			
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
24	10.076	1012	603	0.000	T			
25	10.118	4819	1043	0.000	TV			
26	10.202	7090	1153	0.000	TV			
27	10.490	145219	74597	0.000	TV			
28	10.658	4381	2136	0.000	TV			
29	10.708	4671	2592	0.000	TV			
30	10.969	3797	1319	0.000	T			
31	11.121	1797	469	0.000	T			
32	11.298	1002	319	0.000	TV			
33	11.485	1862	474	0.000	T			
34	12.155	2149	794	0.000				
35	12.290	2461	606	0.000	V			
36	12.662	9603921	1631721	0.000	SV			
37	13.672	1517	695	0.000				
38	13.806	1547	923	0.000				
39	14.672	1248	564	0.000				
Total		55465569	9491795					

APPENDIX D-5

Analysis Date & Time : 7/24/2012 10:53:41 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS11 top  
 Sample ID : PS11 top  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS11 top.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 PS11 top  
 0.4ul

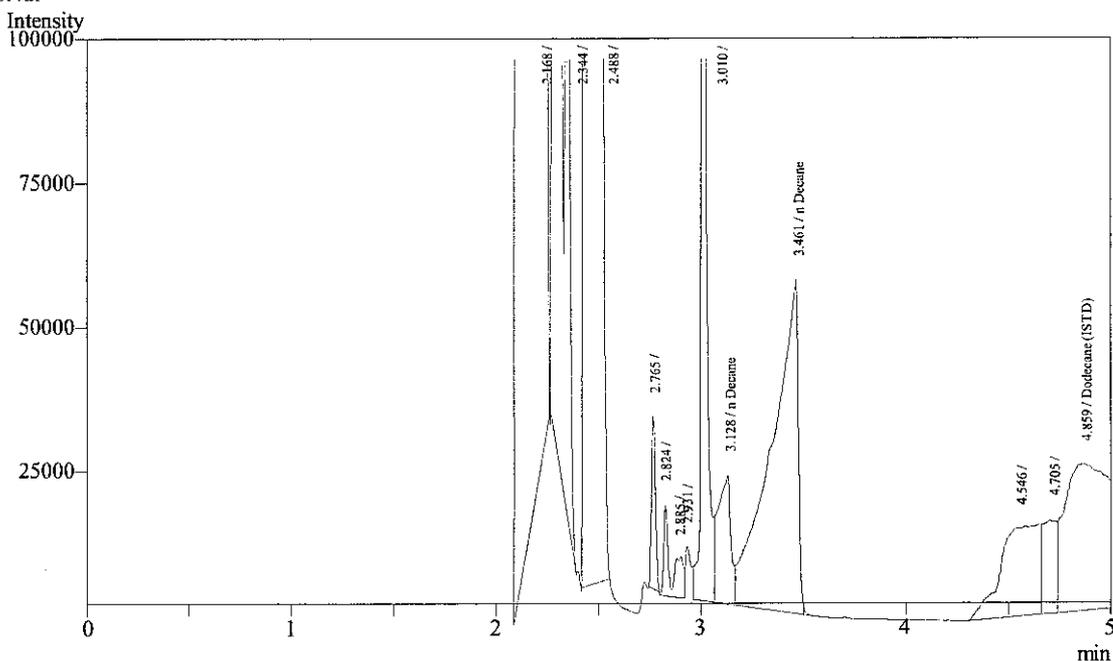


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.227	14915864	4227310	0.000				
2	2.482	9134559	3602653	0.000				
3	2.661	77419	31869	0.000				
4	2.817	30441140	11992519	0.000				
5	2.896	19937	20282	0.000				
6	3.046	18312393	9620916	0.000				
7	3.131	65813	44090	0.000	ug/m		1	n Decane
8	3.339	37374	34795	0.000	ug/m		1	n Decane
9	12.526	3558	1406	0.000				
10	13.139	1358	763	0.000				
Total		73009415	29576603					

APPENDIX D-6

Analysis Date & Time : 7/24/2012 1:33:40 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS11 bot  
 Sample ID : PS11 bot  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS11 bot.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 PS11 bot  
 0.4ul



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.168	4363410	1509035	0.000				
2	2.344	876678	248441	0.000				
3	2.488	12553027	4160834	0.000				
4	2.765	38730	29014	0.000				
5	2.824	22090	15008	0.000				
6	2.885	20177	6719	0.000		V		
7	2.931	17608	8822	0.000		V		
8	3.010	336698	210188	0.000		V		
9	3.128	98003	21932	0.222	ug/m	V	1	n Decane
10	3.461	512682	57163	1.162	ug/m	V	1	n Decane
11	4.546	202798	15378	0.000				
12	4.705	75567	16215	0.000		V		
13	4.859	508348	25360	0.000	ug/m	V	2	Dodecane (ISTD)
14	5.139	58649	19441	0.000		V		
15	5.189	67535	18777	0.000		V		
16	5.260	45709	18183	0.000		V		
17	5.288	366376	17833	0.000		V		
18	7.044	530762	42226	0.000				
19	7.499	505088	76265	0.000		V		
20	7.612	394921	54381	0.000		V		
21	7.946	31710	5918	0.000		V		
22	8.055	16538	4068	0.000		V		

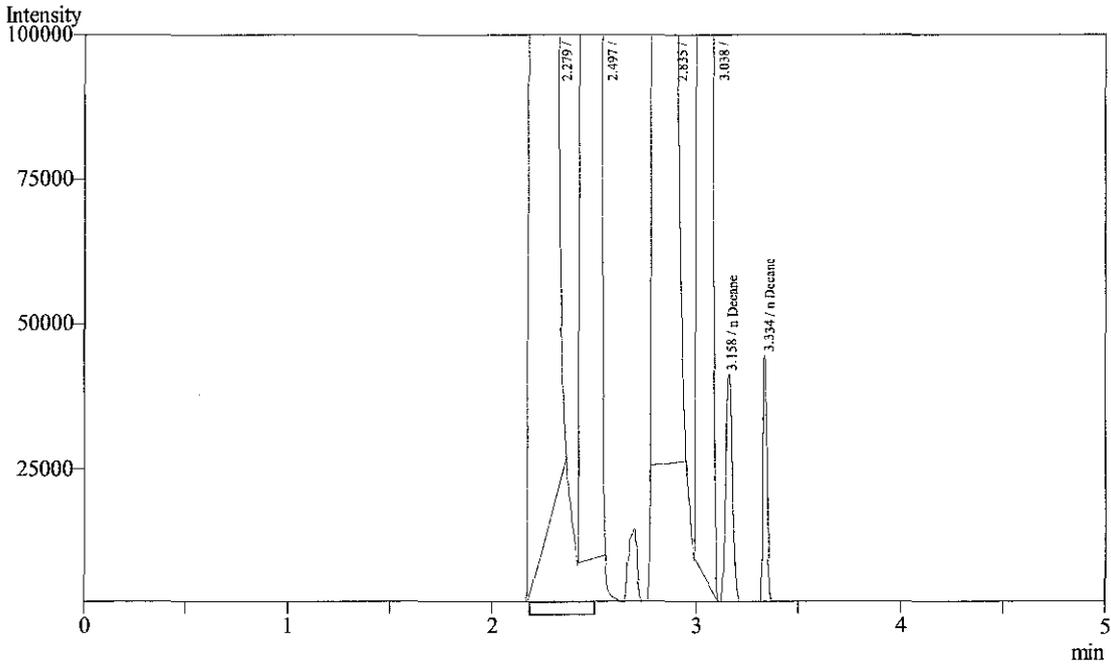
## APPENDIX D-6

23	8.163	18242	7119	0.000	V			
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
24	9.401	11404880	1980662	0.000	S			
25	10.018	2126	1271	0.000	T			
26	10.067	4571	1951	0.000	TV			
27	10.100	4546	2233	0.000	TV			
28	10.132	17472	2680	0.000	TV			
29	10.268	6951	1873	0.000	TV			
30	10.485	104386	47859	0.000	TV			
31	10.656	7261	2746	0.000	TV			
32	10.706	4286	2382	0.000	TV			
33	10.967	1858	802	0.000	T			
34	11.121	1680	417	0.000	T			
35	11.486	2388	491	0.000	T			
36	12.639	7566605	1376214	0.000	S			
Total		40790356	10009901					

APPENDIX D-7

Analysis Date & Time : 7/24/2012 11:27:03 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS12 top  
 Sample ID : PS12 top  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS12 top.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 PS12 top  
 0.4ul

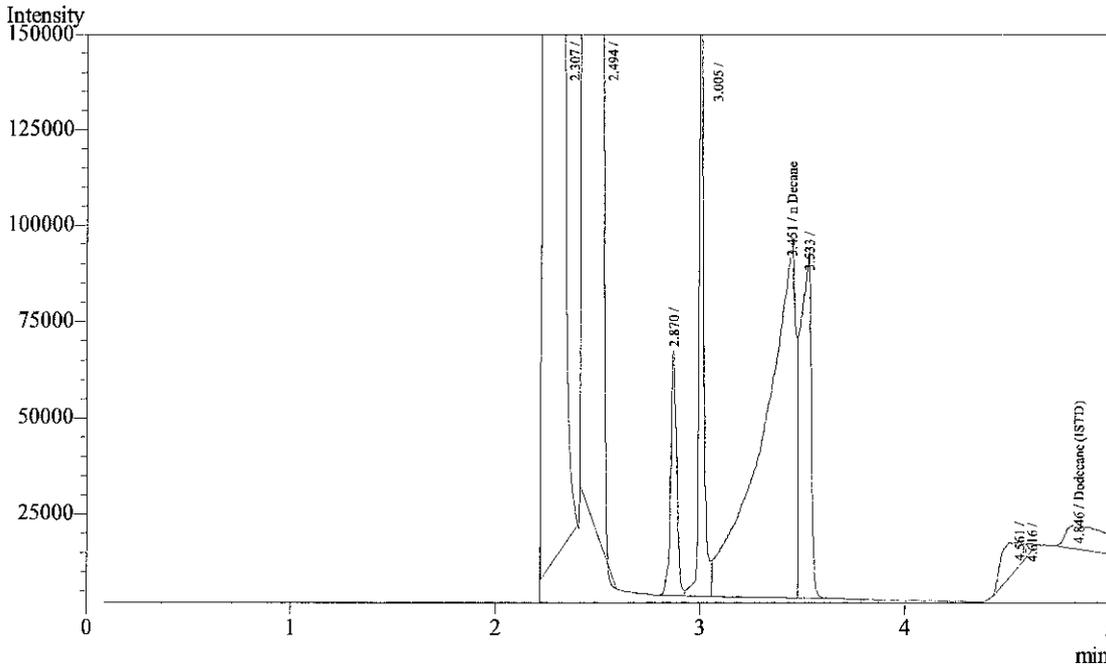


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.279	23012600	5251392	0.000				
2	2.497	15110241	4554813	0.000				
3	2.835	24093644	9051787	0.000				
4	3.038	15780233	8415192	0.000				
5	3.158	93358	39900	0.000	ug/m		1	n Decane
6	3.334	63430	42633	0.000	ug/m		1	n Decane
7	11.130	1110	558	0.000				
8	13.142	5153	2764	0.000				
Total		78159769	27359039					

APPENDIX D-8

Analysis Date & Time : 7/24/2012 2:09:18 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : PS12 bot  
 Sample ID : PS12 bot  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\240712\PS12 bot.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 PS12 bot  
 0.4ul



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Compd Name
1	2.307	9661858	3492950	0.000				
2	2.494	16253272	4716157	0.000				
3	2.870	130289	62787	0.000				
4	3.005	267857	168598	0.000		V		
5	3.451	1012860	93129	13.013	ug/m	V	1	n Decane
6	3.533	334176	88164	0.000		V		
7	4.561	59339	5874	0.000				
8	4.616	5689	2169	0.000		V		
9	4.846	89652	6301	0.000	ug/m		2	Dodecane (ISTD)
10	5.073	58805	5114	0.000		V		
11	5.278	52802	4788	0.000		V		
12	7.063	402035	33176	0.000				
13	7.497	415042	65977	0.000		V		
14	7.610	260973	36322	0.000		V		
15	7.953	24044	4741	0.000		V		
16	8.058	11987	3108	0.000		V		
17	8.166	16403	7102	0.000		V		
18	9.175	2693	1060	0.000				
19	9.386	8468674	1660507	0.000		SV		
20	10.076	1375	585	0.000		T		
21	10.132	4879	901	0.000		TV		
22	10.248	1263	617	0.000		TV		

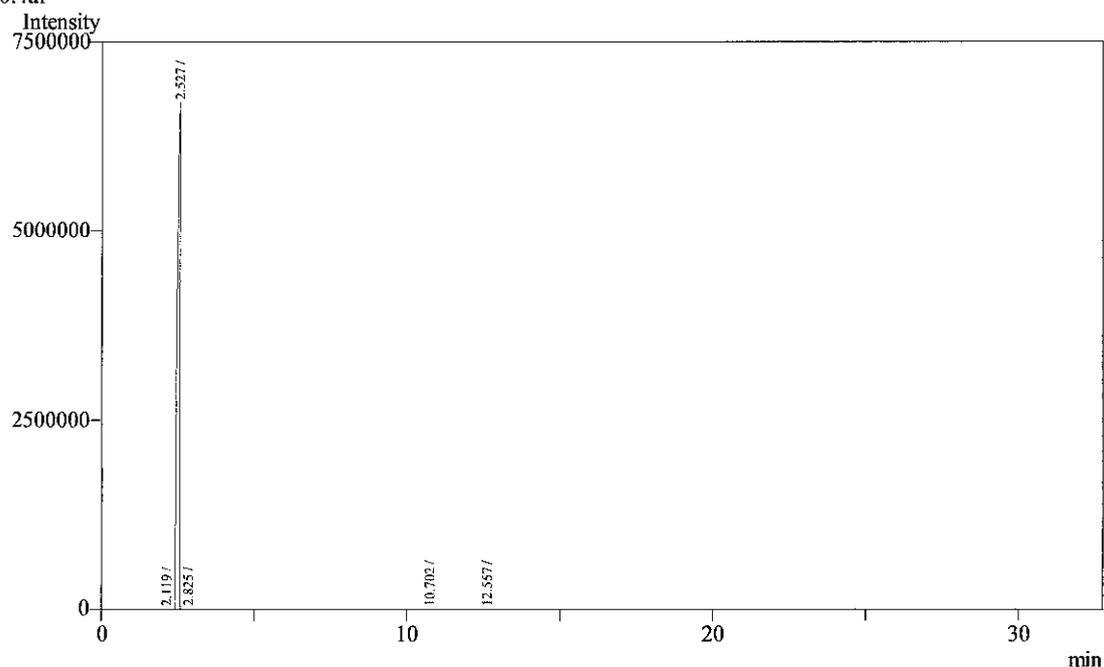
APPENDIX D-8

23	10.487	125877	62693	0.000	TV			
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
24	10.658	8177	3392	0.000	TV			
25	10.708	4171	2234	0.000	TV			
26	10.970	1621	875	0.000	TV			
27	11.121	1521	411	0.000	TV			
28	12.288	1710	635	0.000				
29	12.381	4854	1578	0.000	V			
30	12.639	7388218	1404201	0.000	SV			
Total		45072116	11936146					

APPENDIX E-1

Analysis Date & Time : 7/12/2012 3:15:22 PM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : propanol  
 Sample ID : propanol  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\propanol.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 propanol  
 0.4ul



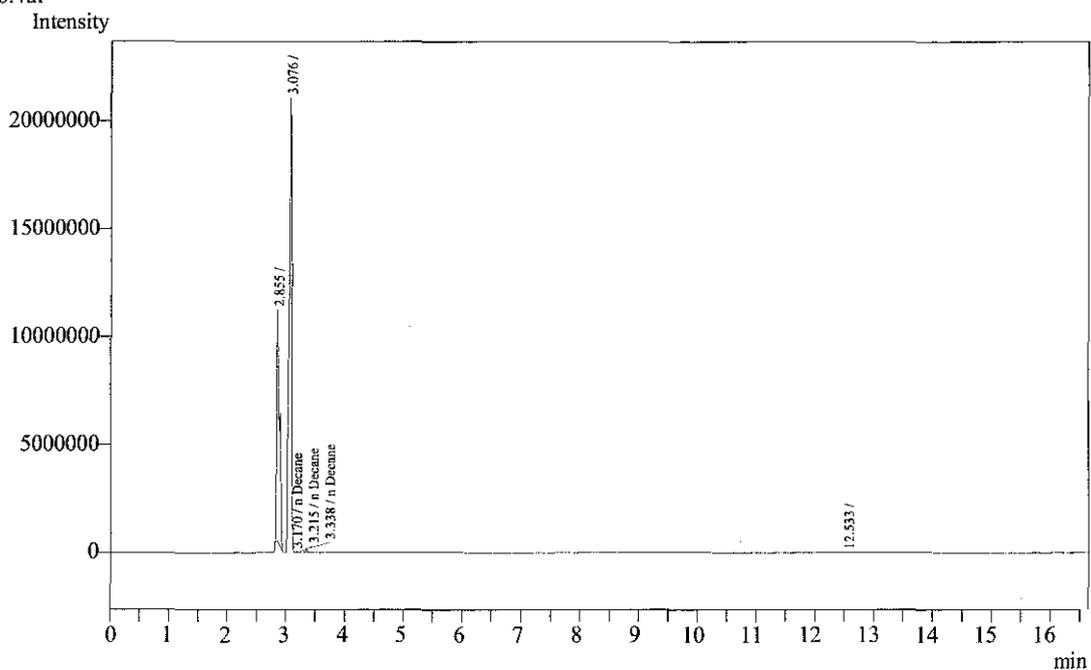
Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	2.119	1715	796	0.000			
2	2.527	39826770	6667501	0.000			
3	2.825	1564	901	0.000			
4	10.702	3271	1020	0.000			
5	12.557	1939	663	0.000			
Total		39835259	6670881				

APPENDIX E-2

Analysis Date & Time : 7/23/2012 10:59:58 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : hexane  
 Sample ID : hexane  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\200712\hexane.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm

[Description]  
 hexane  
 0.4ul



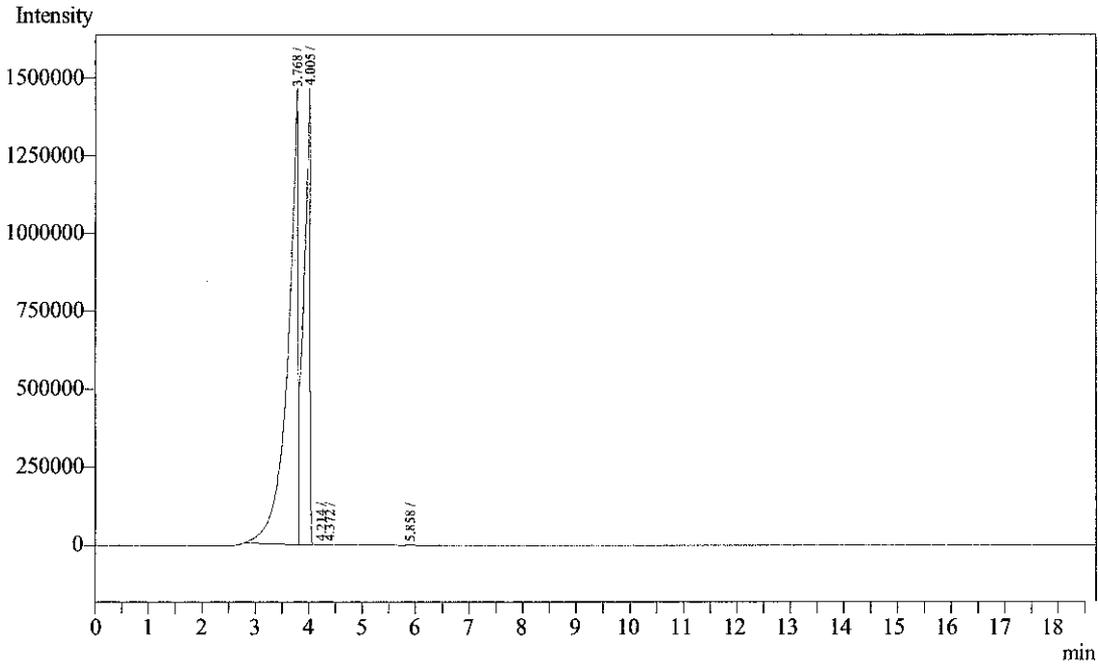
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Compd Name
1	2.855	36276366	10671825	0.000				
2	3.076	63559910	20610250	0.000				
3	3.170	101442	46032	0.000	ug/m	V	1	n Decane
4	3.215	48231	27155	0.000	ug/m	V	1	n Decane
5	3.338	259066	177850	0.000	ug/m		1	n Decane
6	12.533	1134	469	0.000				
Total		100246149	31533581					

APPENDIX E-3

Analysis Date & Time : 7/23/2012 10:22:04 AM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : AA  
 Sample ID : AA  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\200712\AA.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]

AA  
 0.4ul

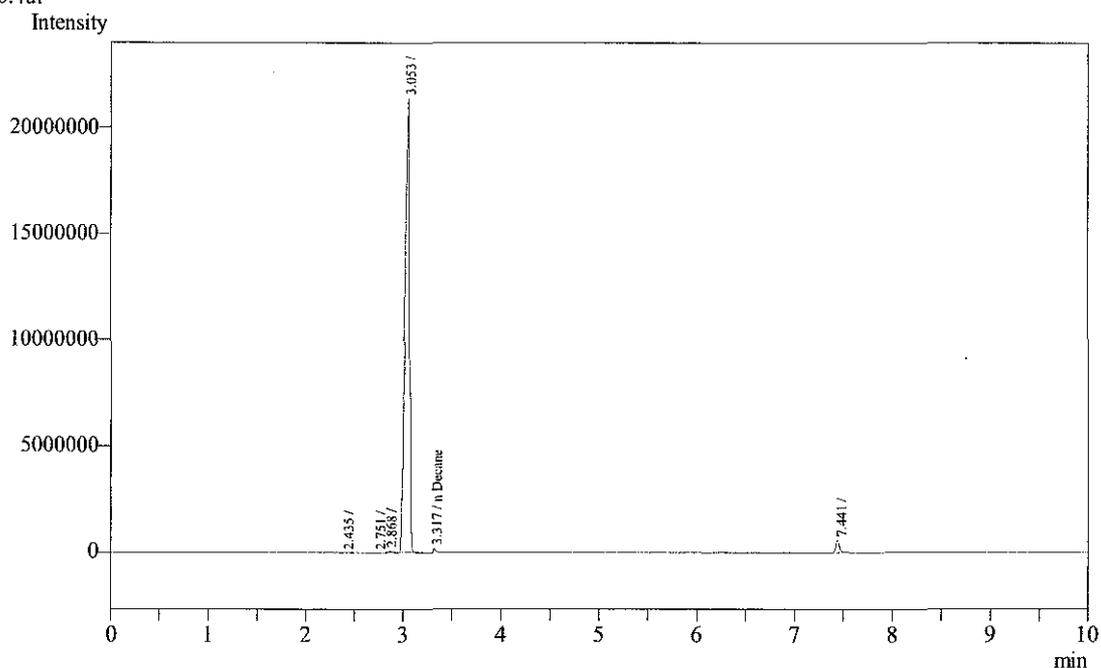


Peak#	Ret. Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	3.768	18216305	1455375	0.000			
2	4.005	11670674	1449673	0.000	V		
3	4.214	9648	2394	0.000			
4	4.372	1345	663	0.000			
5	5.858	1068	469	0.000			
Total		29899040	2908574				

APPENDIX F-1

Analysis Date & Time : 7/20/2012 10:25:17 AM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : phenol hexane  
 Sample ID : phenol hexane  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\200712\phenol hexane.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm  
 [Description]  
 phenol hexane  
 0.4ul



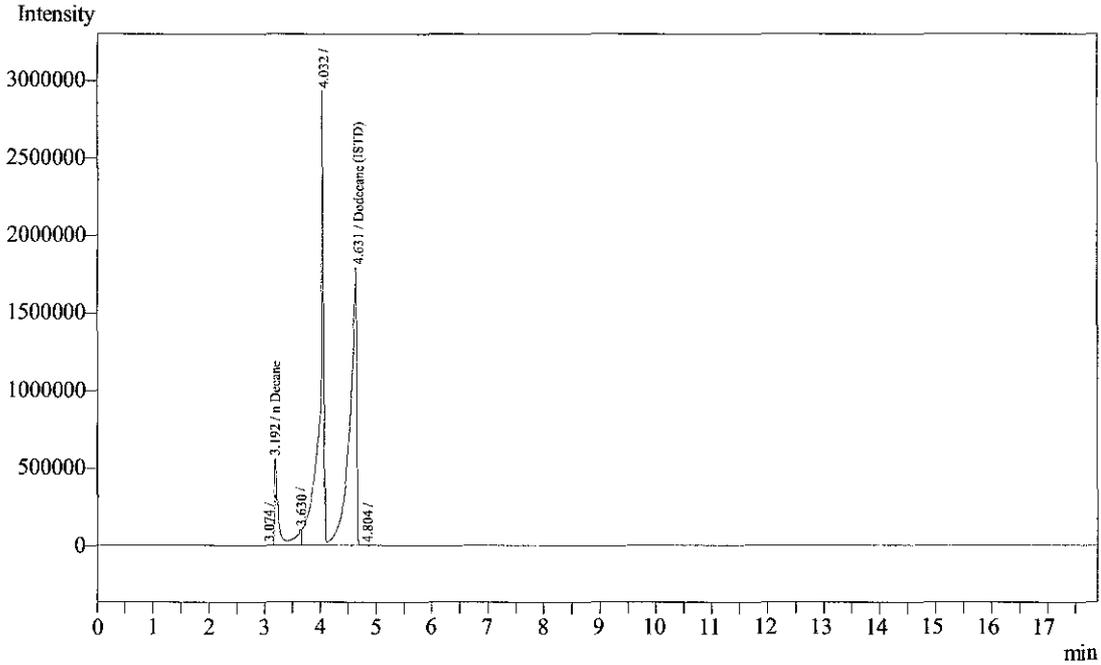
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.435	802	512	0.000				
2	2.751	2050	1336	0.000				
3	2.868	184779	100007	0.000				
4	3.053	68547380	21131578	0.000		S		
5	3.317	289441	199333	0.000	ug/m			1 n Decane
6	7.441	1738092	607189	0.000				
7	10.222	4446	523	0.000				
8	10.673	4836	1208	0.000				
9	12.525	3970	1661	0.000				
Total		70775796	22043347					

APPENDIX F-2

Analysis Date & Time : 7/20/2012 12:47:16 PM  
 User Name : Admin  
 Vial# : 0  
 Sample Name : AA hexane  
 Sample ID : AA hexane  
 Sample Type : Unknown  
 Injection Volume :  
 ISTD Amount : [1]=1

Data Name : C:\GCsolution\Data\hafizah\120712\200712\AA hexane.gcd  
 Method Name : C:\GCsolution\Data\Training 2011\Bio-oil-wissam.gcm

[Description]  
 AA hexane  
 0.4ul



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	3.074	4125	1290	0.000				
2	3.192	2263419	552112	0.178	ug/m	V	1	n-Decane
3	3.630	790310	102017	0.000		V		
4	4.032	14254546	2898413	0.000		V		
5	4.631	14675454	1766976	0.000	ug/m	V	2	Dodecane (ISTD)
6	4.804	7650	1861	0.000		V		
Total		31995504	5322669					