Extraction of Acetic Acid from Bio-oil using Aqueous Salt System

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

____
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UNIVERSITI TEKNOLOGI PETRONAS
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September 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.

NOR ZAITY BINTI CHE MAT ZAKERY

ABSTRACT

Acetic acid surged as high-value chemical due to its wide application in industrial chemical. Acetic acid can be extracted from bio-oil derived from various biomass such as agriculture waste. In this study, the extraction of acetic acid from bio-oil is investigated based on the composition of acetic acid in empty fruit bunch. Liquid – liquid extraction method namely aqueous salt solution is proposed as this method is simple and can be conducted at room temperature. Synthetic bio-oil with composition of acetic acid (10 %), aldehyde (20 %), acetone (10 %), phenol (30 %), and water (30 %) was prepared and characterized. It is found out that the effective phase separation of bio-oil can successfully been conducted through addition of aqueous salt solution. In this study, aqueous ammonium sulphate, $(NH_4)_2\ SO_4$, is used to perform phase separation and the effect of salt concentration on recovery of acetic acid from bio-oil is investigated. Research conducted has revealed that the upper layer mainly contains acetic acid and water-soluble compounds meanwhile the bottom layer consists of water-insoluble, non-polar compound. The acetic acid composition at the upper and lower phase relies on the type and dosage of the salt added. Based on the result, it is found out that the highest amount of acetic acid extracted in upper phase is achieved using 15 % of $(NH_4)_2\ SO_4$ in bio-oil with yield of 25.27 %.

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ABBREVIATION AND NOMENCLATURE

ASTM	American Society for Testing and Materials
CHNS	Carbon, Hydrogen, Nitrogen and Sulfur
EFB	Empty Fruit Bunch
FFB	Fresh Fruit Bunch
GC-FID	Gas Chromatography Flame Ionization Detector
MMTPA	Million Metric Tonnes per Annum
$(NH_4)_2SO_4$	Ammonium Sulphate
PTA	Purified Terephthalic Acid
VAM	Vinyl Acetate Monomer

CHAPTER 1

INTRODUCTION

1.1 Global Demand on Acetic Acid

Overall, world demand for acetic acid is projected to grow at 11.8 million tons in 2015 with strong demand from China, as according to new report by Global Industry Analyst, Inc (GIA). Of total global acetic acid demand, 30% is in China, followed by 27% in Asia, 20% in the United States and 14% in Western Europe. These regions make up 90% of global acetic acid consumption (IHS, 2010).

A major portion of acetic acid is consumed for the production of vinyl acetate monomer (VAM) and Purified Terephthalic Acid (PTA). The derivatives of acetic acid are used extensively in industries like food processing, textiles and adhesive. However, VAM is the largest end use for acetic acid in polymer manufacture for adhesive and coating meanwhile PTA is used mainly for manufacture of polyethylene. In 2010, the global installed capacity of acetic acid was 15.319 million metric tonnes per annum (MMTPA) while the global demand of acetic acid stood at 8.63 MMTPA (Business Wire, 2011). Figure 1.1 shows world consumption of acetic acid:

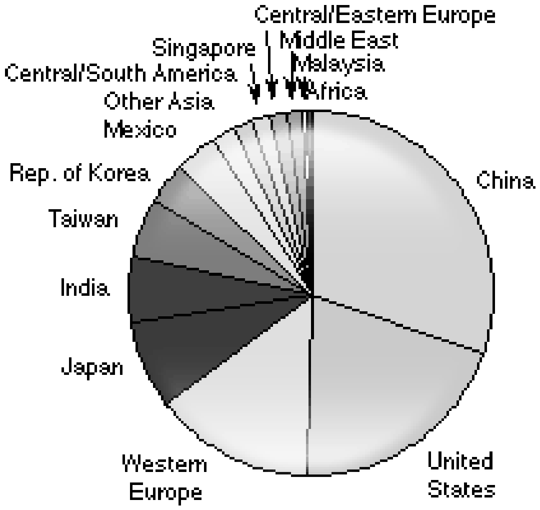


Figure 1.1: World Consumption of Acetic Acid in 2009 (IHS, 2010)

The future growth of acetic acid market will continue to be driven by China (IHS, 2010). Long term global demand for acetic acid is forecast to grow at average annual rate of 3 to 4 % during 2009 to 2014. The key factors driving market growths include global economic scenario and surging demand from end-use segment such as PTA and VAM.

1.2 Bio-oil as a Resource for Acetic Acid

Bio-oils or pyrolysis oils are dark brown, free-flowing organic liquids that comprised of highly oxygenated compounds. Chemically, bio-oil contains a complex mixture of water, catecols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, syringols, guaiacols and other carboxylic acids (Sukiran 2008). Bio-oil also comprises of other major groups of compounds, including, hydroxyketones, sugars, carboxylic acids, hydroxyaldehydes and phenolics (Pizkorz et al., 1988). In all, there are about 400 chemicals in bio-oil which derived from lignin component, acellulose and hemi-celluloses and (Diebold and Bridgewater, 2002; Czernik and Bridgewater, 2005; Ingram et al., 2007).

Bio-oil derived from flash pyrolysis of linocellulosic biomass were found to contain a major component of acetic acid with composition 2-10 wt% (Misson et al., 2009; Ani, 2001) and can be up to 16% Dermibas (2007) and more in various biomass (Xu et al., 2011), thus making the pyrolysis oil very acidic in nature (Dermibas, 2007). In fact, the liquid yields and properties of the pyrolysis oil vary depending on the type of biomass used (Abdullah et al., 2007; Mohan et al., 2006; Azizan et al., 2009; Misson, 2009; Ani, 2001; Aho et al., 2008; Ji-Lu et al.,2008; Dermibas, 2007).

Bio-oils can be produced from various biomasses. These include the source of several forestry i.e. bark rich forest trimming, softwood, hardwood and pine and agriculture feedstock i.e. empty fruit bunch, kernel shell, sugarcane bagasse and wheat straw.

In Malaysia, the abundance of biomass, especially in the form of palm oil waste seems to be the most promising source for bio-oil feedstock. Palm oil waste can be in the form of empty fruit bunch, kernel, trunks, fibre and shells. With production of

18.911 million tonnes of crude palm oil annually MPOB (2012), much of the 92.49 million tons of fresh fruit bunch (FFB) were processed and approximately, 20 million tons of Empty Fruit Bunch (EFB) were generated (MPOB, 2009; Narenberg, 2011). In fact, 19 million metric tonnes of EFB waste generated by palm oil mill end up in landfills (GPA, 2012).

1.3 Recovery Technology of Acetic Acid

There are several recovery techniques that have been introduced to extract acetic acid from bio-oil such as catalytic distillation Zu et al. (1999), anion-exchange resin method Sukhbaatar et al., 2009) and micro emulsion liquid membrane separation (Wiencek and Qutubuddin, 1992). However, due to highly viscous and thermally unstable properties of complex material like bio-oil, none of these techniques seems to be applicable or compatible for the process. Apart from that, the limitations of the other techniques also caused by the presence of large amounts of medium molecular weight compounds ($500 < M_n < 3000$) in pyrolysis oil (Bridgewater et al., 1999). These can cause severe pore blocking of resins and membranes and thus resulting in rapid drop in performance (Bridgewater et al., 1999).

1.3.1 Catalytic distillation

Catalytic distillation is a method which combines the processes of distillation and catalysis in order to selectively separate the mixtures within solution. As reported by Zu et al., (1999), catalytic distillation experiments were conducted using 100 mm diameter column for removal of acetic acid from water. In this process, amberlyst 15 was used as catalyst in order to accelerate the esterification of acetic acid with methanol. The process resulted of more than 50% acetic acid recovered as methyl acetate in the 1.5 meter high test column when the feed contained 2.5 to 9.9 % of acetic acid in water.

Although the end product resulted in high percentage of acetic acid recovery, the distillation process was reported to be costly and development of lower cost separation method is more desirable (Sukhbaatar et al., 2009).

1.3.2 Anion- Exchange Resin Method

Ion-exchange is a term used to describe the process in which water flows through a bed of ion exchange material, whereby undesirable ions are removed and replaced with less objectionable one. Study was conducted by Sukhbaatar et al., (2009) by using anion-exchange resin method to remove acetic acid from bio-oil. Dowex 22, a strong base anion exchange resin was used and regenated by first stirring in NaOH solution and washing with distilled water to obtain quaternary ammonium hydroxide form. The process was conducted in glass column by allowing bio-oil to slowly elute through the ion-exchange resin column by gravity and 10 mL fractions were collected. The result of this method showed pH decreasing from 6.85 to 5.44 as compared to 3.60 for starting solution.

The limitation of this process was due to the uneven elution in small-scale anion-exchange resin column and more quantitative data on the anion-exchange capacity and acid recovery were difficult to obtain. The study also revealed that elution control in small scale become unsatisfactory toward the end of fraction collection.

1.3.3 Liquid-liquid Extraction Method

Liquid-liquid extraction method could be a promising alternative in replacing the existing recovery technology. This technique has been used in extracting the acetic acid from bio-oil. This is because study conducted by (Sukhbaatar et al.,2009; Mahfuz et al., 2008) shows that a simple and low cost technique can be performed through this method.

As compared to other techniques, liquid-liquid extraction method has been shown to obtain 9 to 90 % recovery of acetic acid (Sukhbaatar et al., 2009; Mahfuz, 2009; Rasrendra et al., 2001) . Meanwhile, study conducted by Qin et al.,(2009) shows that salting out effect of ammonium sulphate towards phase separation of acetic acid resulted in mass ratio 78:22 of upper and bottom layer of bio-oil.

1.4 Problem Statement

The successful extraction of acetic acid from bio-oil using common salt is affected by factor such as salt concentration. Therefore, a study needs to be conducted to investigate the effect of salt concentration on the recovery process. Given the suitable concentration of salt with proper technique, this high value chemical can optimally be recovered from aqueous phase of bio-oil at room temperature.

1.5 Objectives

The general aim of this research work is to study the feasibility of recovery of acetic acid from bio-oil using liquid-liquid extraction method. The objectives of this study include:

1. To study potential of recovering acetic acid from bio-oil using ammonium sulphate, $(NH_4)_2SO_4$
2. To investigate the effect of salt concentration on the performance of the liquid-liquid extraction method.

1.6 Scope of Study

The scope of this study covers:

1. Preparation of calibration curve for acetic acid
2. Preparation of aqueous ammonium sulphate, $(NH_4)_2SO_4$ at different concentration
3. Synthetic bio-oil production
4. Characterization of synthetic bio-oil
5. Phase separation of bio-oil using aqueous $(NH_4)_2SO_4$
6. Extraction of acetic acid from bio-oil at room temperature.

1.7 Significant of the Project

The extraction of this acetic acid from pyrolysis oil is a potentially attractive area of research. This is because the study contributes to significant economic potential as acetic acid is an important industrial commodity chemical. In addition, the market price of acetic acid in 2009 is 0.6 USD/kg (Mirasol, 2009) which is remarkably higher that the estimated price for pyrolysis oil with price range of 0.18 to 0.38 USD/kg (Ringer et al., 2006).

1.8 Feasibility of the Project

The overall project is covered within two semesters whereby the first semester focuses on the literature research of bio-oil and relevant extraction process. These include of finding the best type and composition of chemicals for preparing synthetic bio-oil, suitable extractant for separation process with optimum concentration for the process.

The second semester covers all the experimental work whereby the data and evidence collected through literature research is proven. The end result of the experiment is to achieve the maximum yield of acetic acid at optimum salt concentration.

CHAPTER 2
LITERATURE REVIEW

2.1 Bio-oil as Potential Resource for Acetic Acid

The most popular method by which biomass can be converted into bio-oil is by using pyrolysis process (Arami-Neya et al., 2012; Solantausta et al., 2003; Bridgewater et al., 2000; Czernik et al., 2002). Depending on the composition of biomass feedstock and the type of pyrolysis process used, the characteristics of bio-oil can be determined.

However, given the specific composition of chemicals, bio-oil can be prepared synthetically for further study. Fisk et al. (2009) conducted a study using synthetic bio-oil. A mixture of guaicol (17 wt %), de-ionized water (20wt %), methanol (5wt %), acetic acid (14wt %), acetaldehyde (12wt %), glyoxal (4wt %), acetol (8 wt %), glucose (8wt %), furfural (4wt %) and vanillin (8 wt %) were freshly prepared before each experiment. Meanwhile, according to Sukhbaatar et al. (2009), bio-oil derived from various biomass contained 5-10% organic acid, 0-10% ketones and hydroxyketones, 5-20% aldehydes and hydroxyaldehydes, 20-30% phenolics and 15-30% water.

Typically, the production of bio-oil from biomass via pyrolysis process was found to contain carboxylic acid, water, carbohydrates and lignin-derived substances (Mohan et al., 2006; Wild, 2011, Kuoppale et al., 1998). These compounds have properties of acidic, viscous, reactive and thermally unstable which could result in problem of handling and utilization (Zhcnhong et al., 2005; Xiaoyan, 2005; Ronghou, 2005). Various research studies conducted which focusing on how to effectively improve the quality of bio-oil. The simple way of recovery acetic acid in bio-oil is using liquid-liquid extraction technique.

2.2 Reported Studies of Bio-Oil Composition in Biomass

Table 2.1: Reported Studies of Bio-Oil Composition (wt %)

Author	Misson et al.,(2009)	Ani (2001)	Aho et al. (2008)	Ji-Lu et al. (2008)	Dermibas (2007)	Sukhabaatar (2009)	de Haan et al.(2009)	Xu et al.,(2011)
Feedstock	Empty palm fruit bunch (EPFB)		Pine	Cotton stalk	Beech wood	Various biomass	Forest residue	Biomass
Phenolic	23.52	19.96	5.4	–	4.8	20-30	3.9	3.0
Alcohols	3.07	3.47	2	1.88	5.34	-		4.05
Organic acids • Acetic acid • Formic acid • Propionic acid • Butanoic acid	2.32	10.86	4	10.61	16.04	5-10	5.6	20.45
Ketones	0.8	1.38	10.2□	2.95	11.2	0-10	3.5	2.95

Author	Misson et al.,(2009)	Ani (2001)	Aho et al. (2008)	Ji-Lu et al. (2008)	Dermibas (2007)	Sukhabaatar (2009)	de Haan et al.(2009)	Xu et al.,(2011)
Feedstock	Empty palm fruit bunch (EPFB)		Pine	Cotton stalk	Beech wood	Various biomass	Forest residue	Biomass
Aldehydes	0.4	1.6	4	1.23	–	5-20	7.4	2.95
Hydrocarbons	1.31	–	3.2	3.2	–	-	-	1.69
Esters	–	1.25	–	1.75	2	-	-	4.43
Water						15-30		-
Furans	-	-	-	-	-	-	2.1	

2.2 Recovery of Acetic Acid using Chemical Extraction

Bio-oil which containing organic acid, aldehyde and simple phenolic component Ingram et al. (2007) can further be distillated to produce formic acid, acetic acid and other volatile components. These water-soluble fractions of bio-oil resulted in calcium salts of organic acids as precipitate when treated with calcium oxide (Oehr et al., 1993). Other study conducted by Rasrendra et al. (2010) found out that the best result of 86% acetic acid recovery when using tri-n-octylamine (TOA) in 40% of 2-ethyl-hexanol by reactive extraction of pyrolysis oil. Initial separation of bio-oil can be done through addition of little salt such as LiCl, $CaCl_2$, $FeCl_3$, $(NH_4)\ SO_4$, K_2CO_3, and $Fe\ (NO_3)_3$ which will result in water-soluble compound including acetic acid at the upper layer and high viscosity compound at the bottom layer (Qin et al., 2009).

Lower cost separation technique of organic acid such as acetic acid and formic acids and pyrolytic lignin fraction exist in bio-oil was studied by (Sukhbaatar, 2009). The calcium oxide method and a quaternary ammonium anion-exchange resin technique were used as to separate organic acid meanwhile methanol and water used to separate water- insoluble pyrolytic lignin fraction. The study revealed that both techniques were effective in phase separation of bio-oil although further improvement is required.

The removal of carboxylic acids present in bio-oil can be verified through increase of pH of bio-oil from 2.52 to 5.47. This statement was supported through study conducted by Xu et al. (2011) using only calcium oxide, magnesium oxide powder and water which result in aqueous phase in upper phase and heavy oil in bottom phase. According to Sipila et al. (1998), pyrolysis oil can be separated by adding as drop slowly into distilled water in 1:10 weight ratio which forming water soluble and insoluble fraction. The water soluble fraction then further separated using diethylether in 1:1 ratio, producing ether soluble and ether insolubles fraction.

As reported by Sukhabaatar et.al (2009), lignin component can be separated using ethyl acetate as solvent for lignin and sodium bicarbonate for washing out organic acid from solution. This would result in 31% yield of pyrolytic lignin based on bio-oil weight.

Considering factors such as simple, environmental friendly and cost competitive of the process, a systematic liquid-liquid extraction technique can be developed using only common, recyclable and renewable extractants to recover acetic acid.

2.4 Reported Studies on Extraction of Acetic Acid

Table 2.2: Reported Studies on Extraction of Acetic Acid

Author	Biomass	Recovery technique	Process condition	Analysis	Limitation
Mahfuz et al.,(2009)	Beech wood	Liquid-liquid reactive extraction using aliphatic tertiary amines	• 20^{o} C ,	• More than 90wt% of the acetic acid could be extracted in a single equilibrium step	• 10wt% of the TOA ended up in the original BO • BO fraction less attractive for further applications.
Sukhbaatar et al.,(2009)	Pine wood	Direct addition of calcium oxide forming acetic acid and formic acid salt	• pH 7 and 8 • 60^{o}C reduced to room temp. • 4h	• Recovery of acetic acid value 9% and 8.52% based on pH value respectively	• With pH 9 and 10 result in calcium salt of high amount pyrolytic lignin • Unsuited for removal of organic acid
Sukhbaatar et al.,(2009)	Pine wood	Quaternary ammonium hydroxide form (anion-exchange resin)	• pH 6.98 • 2h	• Acetic acid recovery of 8.9 %	• Yield of recovered bio-oil were reasonable but somehow low due to adsorption of bio-oil component on resin particle

Rasrendra et al.,(2011)	Forest residue	Reactive extraction using tri-n-octylamine	• Room temperature	• 86% acetic acid recovery	-
Xu et al.,(2011)	Biomass waste (straw,woodchip)	Addition of equimolar calcium oxide and magnesium oxide. Water added after 3h	• Room temperature • 3.5h	• pH changed from 2.52 to 5.27 in bio-oil	-
Qin et al.,(2009)	Rice husk	Addition of 1ml of 30% ammonium sulphate **(**NH_4) SO_4 solution in 10 ml bio-oil.	• 15^oC • 10 hr	• Result in phase separation - 78: 22 mass ratio of upper and bottom layer in bio-oil	-
Yusof (2011)	Empty fruit bunch	Addition of sodium sulphate (Na_2SO_4) and magnesium sulphate ($MgSO_4$) separately into bio-oil	• Ambient temperature • 24 hr	• (Na_2SO_4) - result in 45.73% of phenol • ($MgSO_4$) – result in 38% of phenol extracted	-

Study conducted by (Yusof, 2011) shows that Zn and K are the least effective compared to Mg and Na in term of salting out effect. Meanwhile, according to Robert (1996), anion sulfate result in more effectiveness in term of salting out effect on protein as compared to chloride.

Table 2.3: Salting out effect of bio-oil (Yusof, 2011)

Anion	Cation	Observation
SO_4^{-2}	Na+	45.73% of phenol extracted
SO_4^{-2}	Mg^{+2}	38% of phenol extracted

Table 2.4: Phase separation of bio-oil using different type of salt (Qin et al., 2009)

Anion	Cation	Molar concentration ,M	Observation, (mass ratio Upper : Bottom)
Cl^-	Li+	2.36	64:36
Cl^-	Li^+	0.64	74:26
Cl^-	Ca^+	0.24	74:26
SO_4^{-2}	NH_4^+	0.21	78:22
$CO^{2-}{}_3$	K^+	0.2	74:26

2.5 Research Gap

The literature research reveals that bio-oil has the potential as a resource for acetic acid. This high value chemical can be recovered using chemical extraction. For selection of the suitable salt solution, ammonium sulphate $(NH_4)_2SO_4$ is proposed as this salt solution is able to give a better result in term of salting out effect as compared to other salt solution. This is in line with Hofmeister series which states that anion sulphate gives larger effect compared to chloride. For cation, ammonium appears to have more salting out effect compared to calcium and lithium.

CHAPTER 3
METHODOLOGY

3.1Research flow

Stage 1: Preparation of standard solution of acetic acid for calibration curve

- Standard solution of pure acetic acid with different concentration (20 to 100 % v/v) were prepared for the purpose of calibration curve.
- Measurement using GC-FID and graph of peak area versus concentration (% v/v) was plotted.

Stage 2: Preparation of aqueous ammonium sulphate, $(NH_4)_2\ SO_4$ as extractant

- Aqueous $(NH_4)_2\ SO_4$ with concentration of 5 to 20 % w/v were prepared as extractant for bio-oil.

Stage 3: Characterization of Bio-oil

- Synthetic bio-oil was prepared before the experiment is conducted and consists of acetic acid (10%), phenol (30%), furaldehyde (20%), acetone (10%) and water (30%).
- Bio-oil was characterized based on viscosity, water content, density, chemical composition, elemental composition, pH and calorific value

Stage 4: Investigation on the effect of salt concentration on phase separation

- Investigation was conducted on the effect of salt concentration on the liquid-liquid extraction method.
- Volume percentage resulted from phase separation of upper and bottom layer of bio-oil is calculated

Stage 5: Recovery of acetic acid from bio-oil

- Concentration of acetic acid at the upper and bottom layer of bio-oil is measured.
- Yield of acetic acid recovered through the process is calculated.

3.2 Experimental Section

3.2.1 Preparation of standard solution of acetic acid

Standard solution of acetic acid with 100 % purity is prepared at concentration of 20 to 100 % v/v. For 20 % v/v, 10ml of pure acetic acid is diluted in distilled water to obtain 50ml of solution. Similar procedure is repeated for the next 40, 60, 80 and 100 % v/v of acetic acid. The standard solution is analysed using GC-FID and graph of peak area versus concentration is plotted. Table 3.1 shows the calculation for overall concentration.

Table 3.1: Dilution for standard solution of acetic acid

Concentration [% v/v]	Acetic acid [ml]	Distilled water [ml]	Total solution [ml]
0	0	50	50
20	10	40	50
40	20	30	50
60	30	20	50
80	40	10	50
100	50	0	50

3.2.2 Preparation of ammonium sulphate, $(NH_4)_2SO_4$ solution

$(NH_4)_2$ SO_4 solution is prepared with different concentration ranging from 5 to 20 %. At 5 % concentration, 5 g of solid $(NH_4)_2SO_4$ with purity of 99.5 % is diluted in distilled water to obtain 100 g of solution. For the next 8, 10, 12 until 20% concentration, the same method is applied. The overall calculation is shown in table 3.2.

Table 3.2: Preparation of ammonium sulphate, $(NH_4)_2$ SO_4 solution

Concentration [%]	$(NH_4)_2SO_4$ [g]	Distilled water [ml]	Total solution [ml]
5	5	95	100
8	8	92	100
10	10	90	100
12	12	88	100
14	14	86	100
15	15	85	100
16	16	84	100
20	20	80	100

3.2.3 Synthetic bio-oil production

Synthetic bio-oil is prepared before the experiment is conducted and consisted of a mixture of acetic acid (10%), phenol (30%), acetone (10%), furaldehyde (20%) and de-ionized water (30%). The composition was chosen based on the study conducted by (Sukhbaatar et al., 2009) on typical pyrolysis oil derived from various biomass and acetic acid composition is chosen to reflect the composition in biomass (Misson et al., 2009; Ani, 2001). 100 ml of synthetic bio-oil is produced by mixing the chemicals altogether with their respective volume. The experimental work is done under fume hood and at room temperature, 25^{o}C. Synthetic bio-oil produced is kept in glass ware with cap (150ml) and stored in refrigerator to avoid volatility of this product. Table 3.3 summarized the purity of each chemical, concentration, mixing volume and brand.

Table 3.3: Purity, concentration, mixing volume and brand of each chemical

Chemical	**Purity [%]**	**Concentration [%]**	**Mixing volume**	**Brand or Supplier**
Acetic acid	100	10	10	Merck
Phenol	98	30	30	R.M. Chemical
2-Furaldehyde	99	20	20	Fisher
Acetone	99	10	10	Merck
De-ionized water	-	30	30	-

3.2.4 Physicochemical characterization

100 ml of synthetic bio-oil prepared is stirred using magnetic stirrer at 400 rpm for 2 hours to form homogeneous mixture. The sample is then characterized based on the physicochemical properties such as density, pH value, water content, calorific value and viscosity using standard ASTM method. The elemental composition (carbon, hydrogen and nitrogen) is analysed using CHNS analyzer.

Table 3.4: Standard method used for characterization

Physical Properties	Standard / Method	Equipment
Water Content	ASTM E 203-96 / Volumetric Karl Fisher Titration	Karl-Fisher Meter
Viscosity	ASTM D 445	Viscometer
pH number	-	pH meter
Higher Heating Value (HHV)	DIN 51900	Bomb calorimeter
Density	ASTM D 4052	Density meter
Element Composition	ASTM D 5291	LECO CHN600

3.2.5 Phase separation of bio-oil

Phase separation of bio-oil is performed with addition of 1ml of aqueous $(NH_4)_2 SO_4$ at different concentration into 10ml of bio-oil. 8 samples consist of 10ml of bio-oil each, were placed in glass tube (15ml capacity and 15mm in diameter). Afterward, each sample is added with 1ml of 5, 8, 10, 12, 14, 15, 16 and 20 % of aqueous $(NH_4)_2 SO_4$. Samples were then shake using water bath shaker for 24 hours at 200 rpm, with temperature of 25^{o}C. After that, all the samples were stored at room temperature for 3 hours to ensure good phase separation. The procedures conducted follow the same procedure conducted by Vitasari et al., (2011) on the water extraction of pyrolysis oil. Figure 3.1 to 3.5 below show the procedure of conducting the experiment.

Figure 3.1: Preparation of synthetic bio-oil

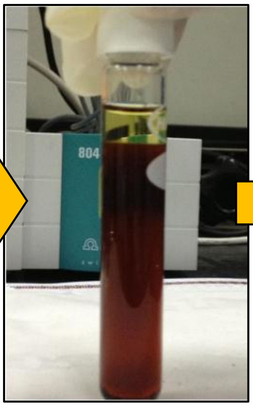


Figure 3.2: 10ml of bio-oil in 15ml test tube

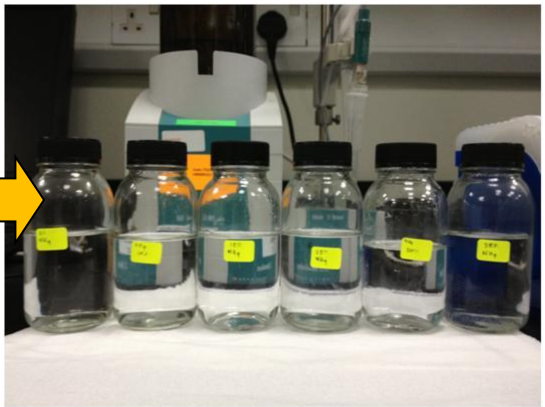


Figure 3.3: Aqueous $(NH_4)_2$ SO_4 at 5, 8, 10, 12,14,15,16 and 20 % w/v. 1ml of (NH_4) SO_4 at each concentration is added with 10ml bio-oil

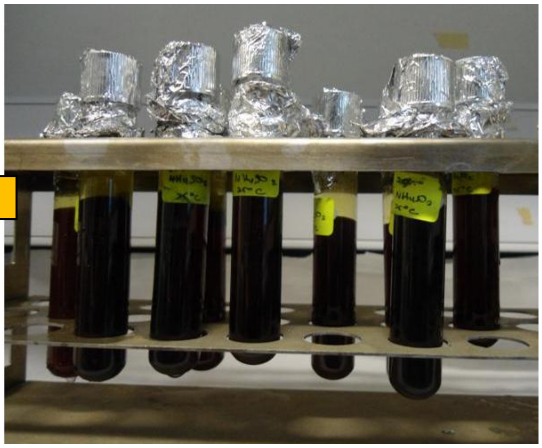


Figure 3.4: Mixtures were shake in water bath shaker for 24 hours, 200rpm at 25 ^{o}C.

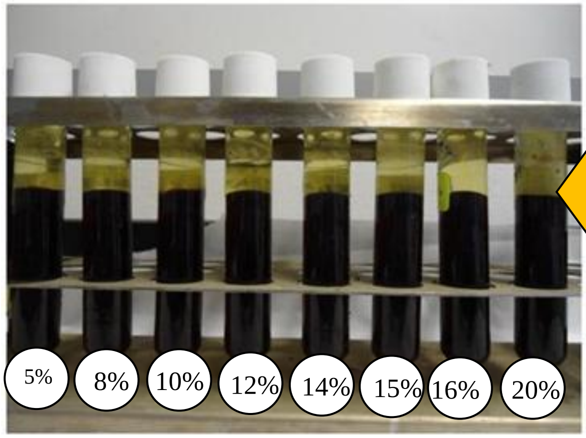


Figure 3.5: Samples were stored at room temperature for 3 hours

3.2.6 Extraction of acetic acid from bio-oil using aqueous salt system

The upper, middle and bottom layer formed through addition of aqueous $(NH_4)_2\ SO_4$ at concentration of 5 to 20 w/v % were extracted using syringe. Samples were then weighted to get the ratio between upper and bottom phase. Comparison is made between the concentrations of $(NH_4)_2\ SO_4$ and the ratio obtained. Volume percentage for each phase is determined by:

$$\text{vol}\ \% = \frac{v\ phase}{v\ _{BO}}\ x\ 100 \tag{1}$$

Where:

$v\ phase$ = volume of sample in the respective phase after extraction
$v\ _{BO}$ = volume of the overall bio-oil after addition of aqueous $(NH_4)_2SO_4$

Afterwards, samples at each phase is analysed using GC-FID to get the concentration of acetic acid. GC-FID type Shimadzu, Model GC-2010 equipped with capillary column (30 m x 0.25 mm x 0.25 µm) and helium as carrier gas was applied. GC- FID conditions were as followed: injector temperature 250^{o}C; oven temperature 120 ^{o}C – 200 ^{o}C; detector temperature 260 ^{o}C and heating rate 15 ^{o}C / min. In this paper, the amount of acetic acid extracted in the upper and bottom phase based on the initial amount in bio-oil is defined as yield % and given by:

$$\text{yield}\ \% = \frac{m_{AA}}{m_{BO}}\ x\ 100 \tag{2}$$

Where:

$m\ phase$ = amount of acetic acid(ml) in each phase (upper and bottom) after extraction
$m\ BO$ = amount of acetic acid (ml) in the original synthetic bio-oil before extraction

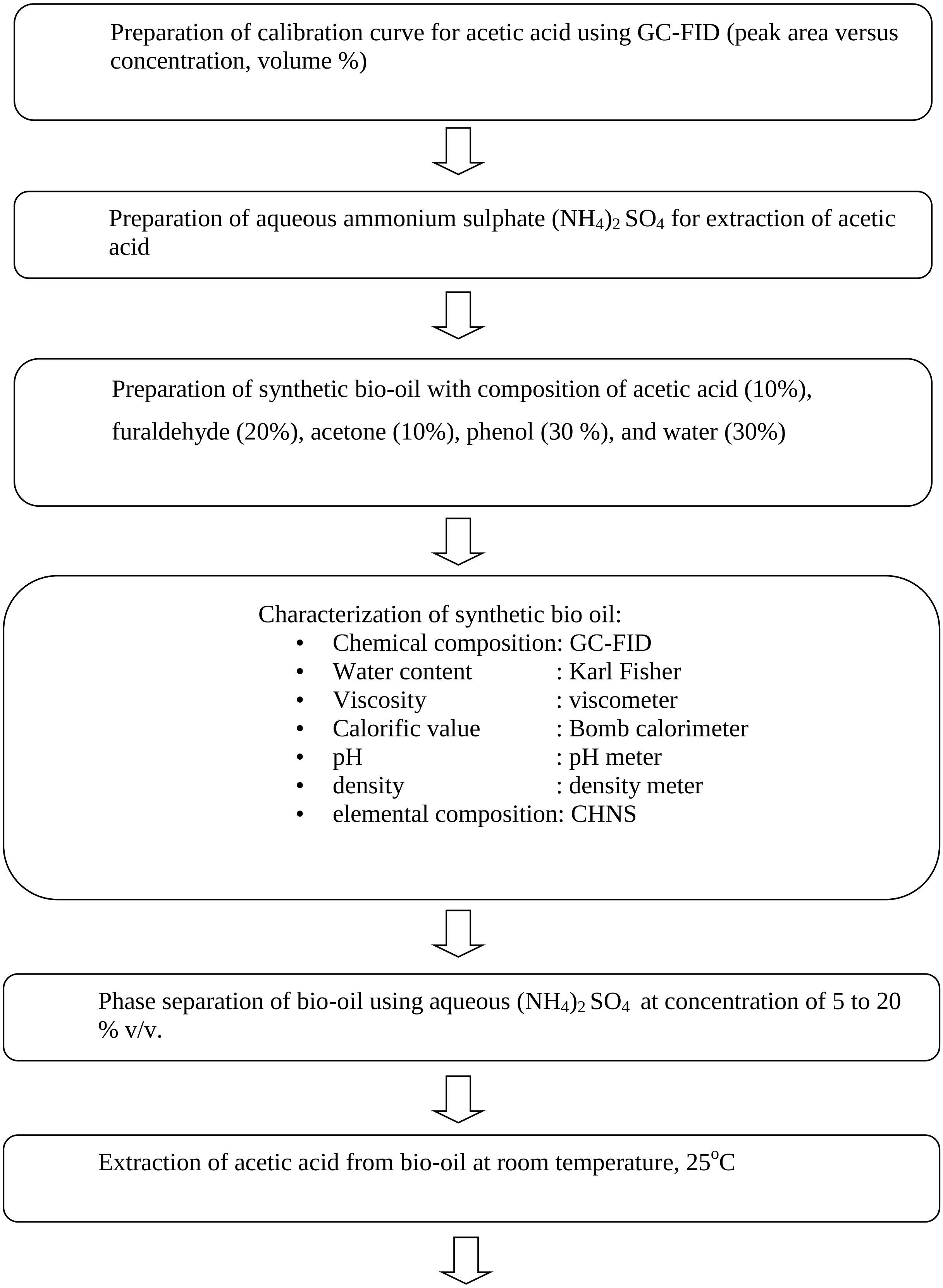
Another measure for extraction performance can also be determined through distribution coefficient (K_D). Distribution coefficient is defined as the ratio of the amount of acetic acid in the aqueous extract phase and the amount of acetic acid in the organic phase.

$$K_D = \frac{x_U}{x_B} \qquad (3)$$

Where:

x_U = amount of acetic acid (ml) in the upper phase after extraction
x_B = amount of acetic acid (ml) in the bottom phase after extraction

Figure 3.5 summarized the experimental procedure



Preparation of calibration curve for acetic acid using GC-FID (peak area versus concentration, volume %)

Preparation of aqueous ammonium sulphate $(NH_4)_2SO_4$ for extraction of acetic acid

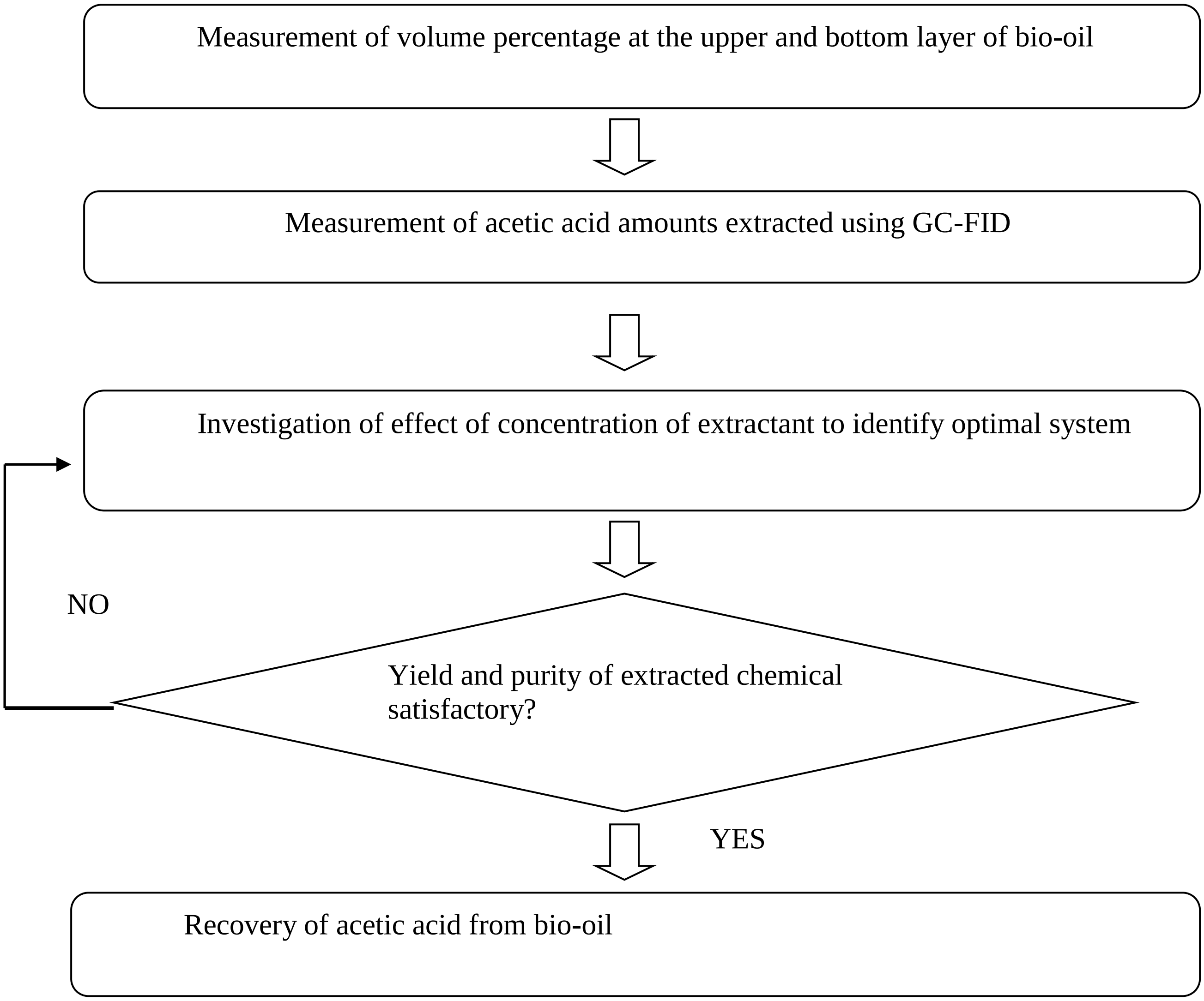
Preparation of synthetic bio-oil with composition of acetic acid (10%), furaldehyde (20%), acetone (10%), phenol (30 %), and water (30%)

Characterization of synthetic bio oil:

- Chemical composition: GC-FID
- Water content : Karl Fisher
- Viscosity : viscometer
- Calorific value : Bomb calorimeter
- pH : pH meter
- density : density meter
- elemental composition: CHNS

Phase separation of bio-oil using aqueous $(NH_4)_2SO_4$ at concentration of 5 to 20 % v/v.

Extraction of acetic acid from bio-oil at room temperature, 25°C



Measurement of volume percentage at the upper and bottom layer of bio-oil
Measurement of acetic acid amounts extracted using GC-FID
Investigation of effect of concentration of extractant to identify optimal system
NO
Yield and purity of extracted chemical satisfactory?
YES
Recovery of acetic acid from bio-oil

3.3 Gantt Chart

Table 3.5: Gantt Chart for Final Year Project

Project Activities	Final Year Project I															
	Week															
	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
Topic selection	■	■						Mid Semester Break								
Literature study • Bio-oil • Acetic acid • Recovery technology	■	■	■	■	■											
Identification of suitable extractant			■	■	■											
Identify composition of chemicals for synthetic bio-oil		■	■	■	■											
Development of experimental procedures		■	■	■	■											
Submission of Extended Proposal Defence						■										
Proposal defence									■	■						
Submission of interim draft report											■	■	■	■		
Submission of interim report														■	■	

Table 3.6: Gantt Chart for Final Year Project II

Project Activities	**Final Year Project II**														
	Week														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Preparation of calibration curve	■	■	■												
Preparation of $(NH_4)_2 SO_4$ solution			■	■											
Synthetic bio-oil production				■	■										
Characterization of synthetic bio oil					■	■	■	■							
Progress report							■	■							
Phase separation of bio-oil					■	■	■	■	■	■	■	■			
Extraction of acetic acid from bio-oil					■	■	■	■	■	■	■	■			
Measurement of mass percentage at the upper and bottom layer					■	■	■	■	■	■	■	■			
Measurement and characterization of acetic acid amounts extracted					■	■	■	■	■	■	■	■			
Pre-Edx					■	■	■	■	■	■	■				
Optimal liquid-liquid extraction method												■			
Draft report										■	■	■			
Dissertation (soft bound)											■	■	■		
Technical paper												■	■		
Project dissertation (hard bound)												■	■	■	■

3.5 Equipment and tools

Table 3.7 and 3.8 summarized the list of equipment and tools used for the experimental work.

Table 3.7: List of equipment required for characterization of bio-oil

Equiment	Model	Specification
Karl-Fisher Meter	870 KF Titrino plus	Unit : %
Viscometer	Brookfield CAP 2000+ Viscometer	Unit: centipoises (cP) Speed: 300 rpm
pH meter	Portable pH meter	-
Bomb calorimeter	Bomb calorimeter C5000	Unit: MJ/ kg
Density meter	Density meter DMA 4500	Unit; g/cm^3
GC-FID	Shimadzu, Model GC-2010	-Capillary column (30mx0.25mm), - Film thickness, 0.25μm - Temperature of injector; 250ºC, - Temperature of oven; 120-200ºC - Temperature of detector; 260ºC. - Carrier gas: helium
CHNS analyser	CHNS 932	Unit : % Analyse carbon, hydrogen, nitrogen and oxygen
Magnetic stirrer	Magnetic stirrer	400 rpm, 2 hours
Water bath shaker	Water bath shaker	25 ^{o}C

Table 3.8: List of tool required for experimental work

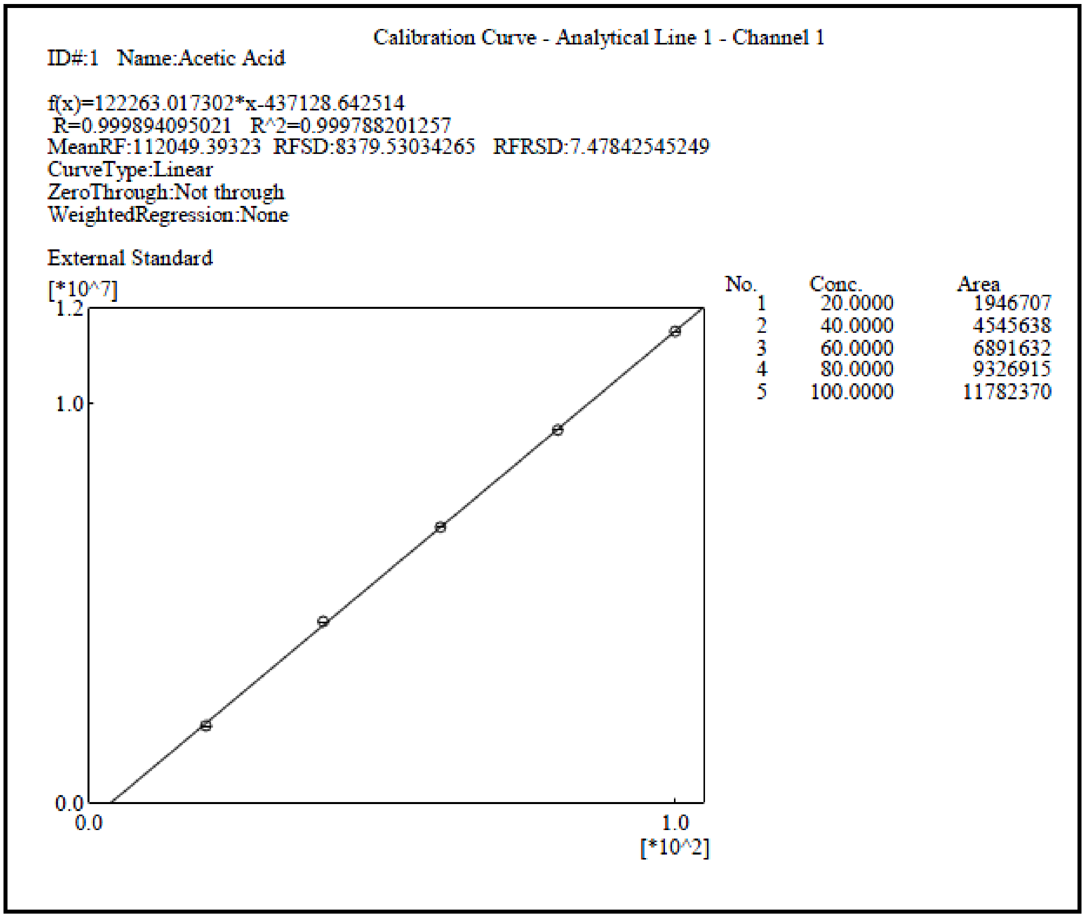
Tools	Specification	Function
Test tube	15 ml capacity, 15mm in diameter	Phase separation of bio-oil
Syringe	10 ml	For the extraction of upper phase of bio-oil
Beaker	250 ml	Preparation of bio-oil, $(NH_4)_2 SO_4$ and acetic acid
Measuring cylinder	10ml, 100ml	Preparation of bio-oil, $(NH_4)_2 SO_4$ and acetic acid
Conical flask	250 ml	Preparation of bio-oil
Glass bottle with cap	30ml, 150ml	Store acetic acid, $(NH_4)_2 SO_4$ and bio-oil

CHAPTER 4

RESULT AND DISCUSSION

4.1 Calibration curve of acetic acid

Calibration curve of acetic acid is prepared at the beginning of experiment. This curve is used as reference to determine the acetic acid concentration in upper and bottom phase of bio-oil. The graph is plotted automatically using software in GC. Different concentrations of acetic acid (0, 20, 40, 60, 80 and 100 % v/v) are used to establish the calibration curve. Distilled water is used as blank with concentration of 0% v/v in the graph. The standard solution is analyzed using GC- FID and graph of peak area versus concentration is plotted. The graph obtained is linear with the concentration range 0 to 100 % v/v of acetic acid target.



```
                         Calibration Curve - Analytical Line 1 - Channel 1
ID#:1   Name:Acetic Acid

f(x)=122263.017302*x-437128.642514
 R=0.999894095021   R^2=0.999788201257
MeanRF:112049.39323  RFSD:8379.53034265   RFRSD:7.47842545249
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard
```

```
No.     Conc.        Area
 1       20.0000      1946707
 2       40.0000      4545638
 3       60.0000      6891632
 4       80.0000      9326915
 5      100.0000     11782370
```

Figure 4.1: Calibration curve of acetic acid

4.2 Physicochemical characterization of bio-oil

Physicochemical properties of bio-oil is analyzed based on pH, water content, density, viscosity, heating value and elemental composition. Table 4.1 shows the physicochemical properties of synthetic bio-oil

Table 4.1 Physicochemical properties of synthetic bio-oil used in this work

Properties	**Synthetic bio-oil used in this work**
Water content (%)	30
Density (g/ cm$^{3)}$	1.0458
Viscosity (cP)	32.6
Heating value (MJ/ kg)	15.873
pH	2.22
Elemental composition (%)	
C	40.62
H	7.562
N	0.172
S	0.412
O	51.234

Table 4.1 shows the properties of synthetic bio-oil used in this work. The high water content of bio-oil reflects the low viscosity and low heating value of this compound. Low carbon and hydrogen percentage also reflect the low heating value of bio-oil. Meanwhile, for pH, the value is very low which indicate that this compound is very acidic. This is in line with study conducted by Mahfuz et al. (2008) which reported that bio-oil is very acidic in nature due to existence of organic acid.

4.3 Phase separation of bio-oil using aqueous salt

Addition of 1 ml of aqueous $(NH_4)_2SO_4$ at concentration of 5 to 20 % w/v resulted in phase separation of bio-oil. The upper layer exhibit mostly water soluble compound meanwhile the bottom layer contain organic, non-polar compound. The ratios between both phases are calculated based on volume percent. Figure 4.2 shows the phase separation of bio-oil at different concentration of aqueous $(NH_4)_2SO_4$.

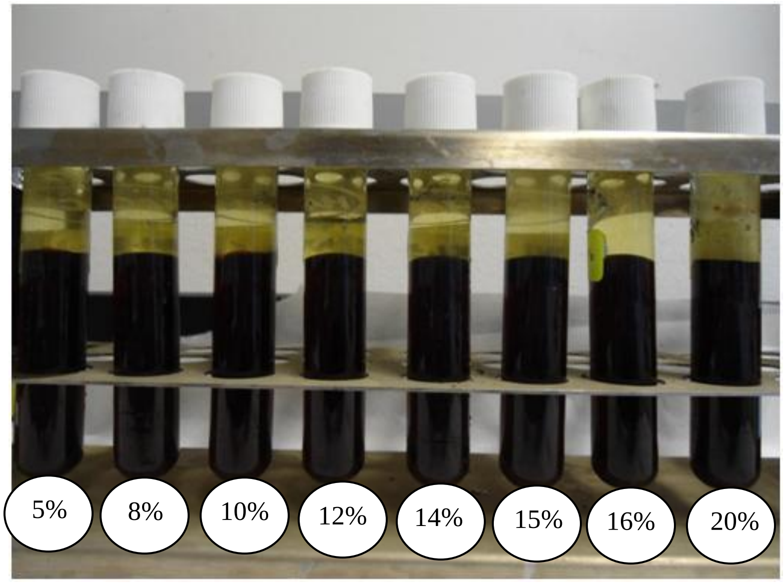


Figure 4.2: Phase separation of bio-oil at 5, 8, 10, 12, 14, 15, 16 and 20 % w/v of aqueous $(NH_4)_2SO_4$

Based on the figure, it is observed that phase separation occurred in bio-oil and the distribution between upper and bottom layer in each salt concentration is almost similar. This might due to composition of synthetic bio-oil which contains mostly water and thus making it readily separates at the beginning of experiment. When salt is added, there is only a slight difference in the phase separation depending on the salt dosage. The exact amount of upper layer extracted using 3ml syringe and the result is obtained through calculation of volume percentage. Comparison is made between the concentrations of aqueous $(NH_4)_2SO_4$ with volume percentage obtained. Based on the result, as the concentration gets higher, the ratio between upper layer to bottom layer increased but in smaller amount. This results obtained is in line with the research conducted by Qin et al.,

(2009) which stated that the phase separation is increasing as the salt concentration increased. Table 4.2 summarizes the result of volume ratio for 5 to 20 % w/v of $(NH_4)_2SO_4$.

Table 4.2: Volume percentages at different concentration of aqueous $(NH_4)_2SO_4$

$(NH_4)_2SO_4$ (w/v %)	Upper (mL)	Bottom (mL)	Upper (vol %)	Bottom (vol %)	Ratio U:B
5	2.6	8.4	24	76	24:76
8	2.7	8.3	25	75	25:75
10	2.8	8.2	25	75	25:75
12	2.8	8.2	25	75	25:75
14	2.9	8.1	26	74	26:74
15	3	8	27	73	27:73
16	3	8	27	73	27:73
20	3	8	27	73	27:73

U: upper layer, B: bottom layer

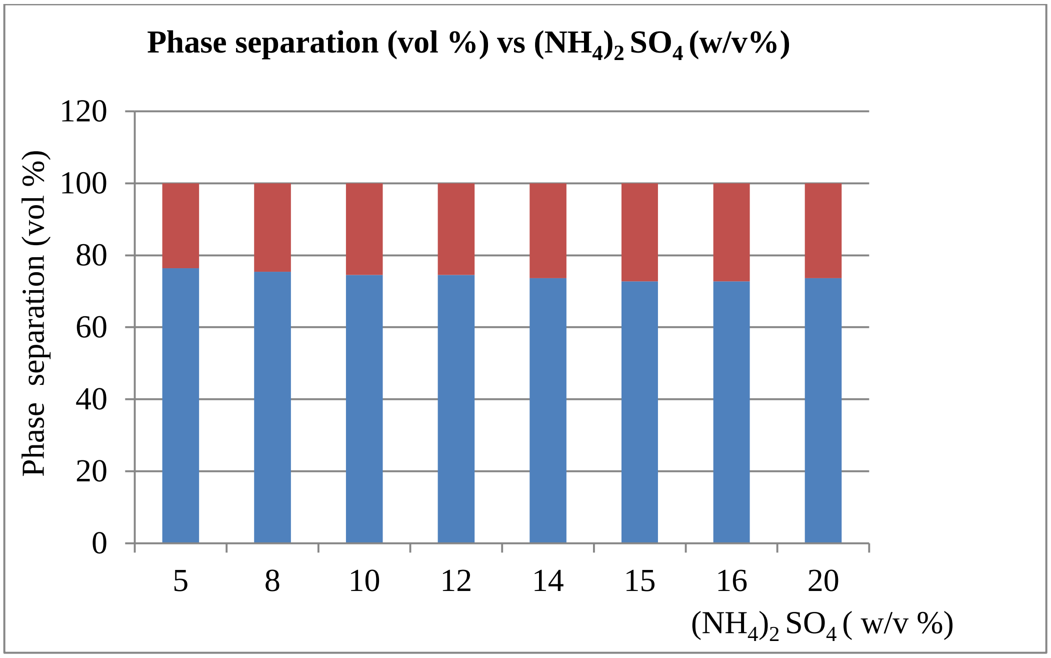


Figure 4.3: Phase separation (volume %) versus aqueous $(NH_4)_2SO_4$ (w/v %)

4.4 Extraction of acetic acid

The concentration of acetic acid in upper and bottom layer at 5, 8, 10, 12, 14, 15, 16 and 20 % w/v of aqueous $(NH_4)_2 SO_4$ are analyzed using GC-FID. The peak areas indicate the amount of compound contained in the aqueous phase of upper layer and organic phase of bottom layer. Based on the result, it shows that the peak area of acetic acid in upper layer is 24 % and bottom layer contained mostly phenol with peak area of 60%. Table 4.3 shows the peak area of acetic acid and phenol at upper and bottom layer of bio-oil using 5% w/v of aqueous $(NH_4)_2 SO_4$. Figure 4.4 and 4.5 shows the ions chromatography of bio-oil in upper and bottom layer respectively.

Table 4.3: The peak area of acetic acid and phenol at upper and bottom layer of bio-oil.

Compound	Peak area (%)
Acetic acid	24 (upper layer)
Phenol	60 (bottom layer)

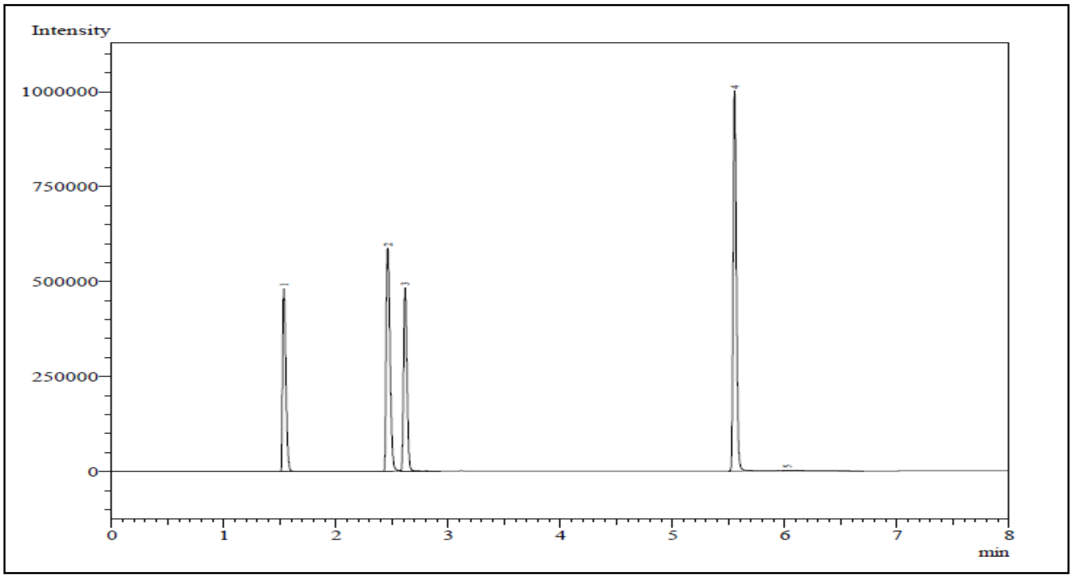


Figure 4.4: Ions chromatography of upper layer using 5 % w/v of aqueous $(NH_4)_2 SO_4$

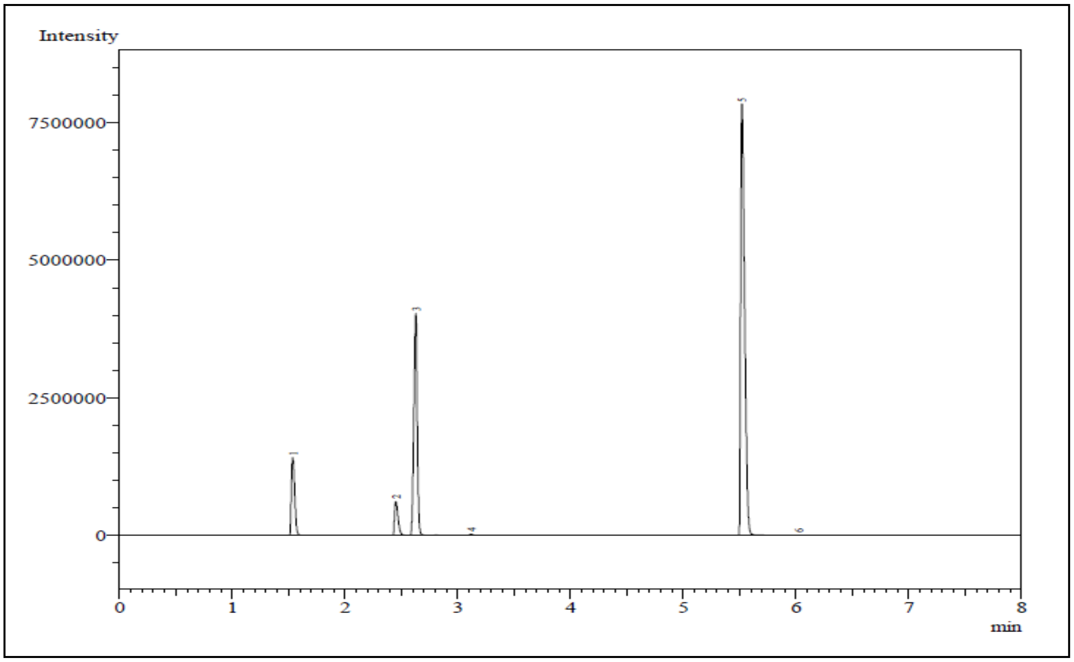


Figure 4.5: Ions chromatography of bottom layer using 5 % w/v of aqueous $(NH_4)_2 SO_4$

The results obtained at the upper and bottom layer is analysed after addition of 5 % w/v aqueous $(NH_4)_2 SO_4$. At the upper layer, it shows that the concentration of acetic acid at retention time of 2.463 is with 9.68 %. Meanwhile, the concentration of phenol at the upper layer is 3.8 %. For the bottom layer, the concentration of acetic acid is 9.21 % at retention time of 2.453 and the concentration of phenol is much higher at retention time of 5.542 which is 37.18 %. The concentration obtained is based on calibration curve.

This happen because the upper layer contains water-soluble compound meanwhile the bottom layer exhibits non-polar of organic compound. As according to Qin et al., (2009), some high-polarity compound have the higher proportion upper layer compared to bottom layer such as ketones, alcohol etc. Bottom layer consist of mostly lignin-pyrolysis compounds such as phenol, 4-hydroxy-3-methoxy-cinnamic acid methyl ester etc.

Further study is conducted to determine the optimum concentration of aqueous $(NH_4)_2 SO_4$ which gives the highest amount of acetic acid at the upper phase. With addition of

1ml of 5 to 20 % w/v aqueous $(NH_4)_2 SO_4$ into 10 ml of bio-oil, the result is analysed using GC-FID. Table 4.4 summarized the amount of acetic acid at the upper phase and bottom phase based on the concentration calibrated on standard curve.

Table 4.4: Amount acetic acid at upper and bottom layer

$(NH_4)_2SO_4$ (% w/v)	Concentration (%)		Amount (mL)	
	Upper phase	Bottom phase	Upper phase	Bottom phase
5	9.6754	9.2069	0.25156	0.77338
8	9.6862	9.3133	0.261527	0.773004
10	9.4983	9.2494	0.265952	0.758451
12	9.4834	9.2126	0.265535	0.755433
14	9.3935	9.2319	0.272412	0.747784
15	9.4226	9.3961	0.282678	0.751688
16	9.3069	9.399	0.279207	0.75192
20	9.2808	9.5016	0.278424	0.760128

The result shows that with addition of salt, only a small amount of acetic acid managed to be extracted. This is because, the original bio-oil contains high value of water, thus causing phase separation at beginning. Much overlap of compound type exist in both fraction which resulted in further difficulty of separation. As the salt concentration increased, a slightly increment in the amount of acetic acid is extracted in upper phase. The reason is when salt is added into bio-oil, it causes precipitation of the organic compound by destroying hydrogen bond and dispersing the bridging component. The reaction causes agglomerization and separation of the organic compound. The water-insoluble compound with low polarity will separate from aqueous phase and agglomerate with organic compound leading it to settle to bottom. Water-soluble compound such as acetic acid will goes to the top and water- insoluble compound such as phenol will goes to the bottom. The highest amount of acetic acid extracted is obtained at 15 % w/v with 0.28 ml in comparison to 1ml of acetic acid in the raw bio-oil.

The process occurs is similar with salting out effect of protein. However, further increment of salt concentration beyond 15 % w/v causes the amount of acetic acid to be decreased at upper layer. This might due to increase in molecular weight, causing the aqueous phase to settle at bottom and organic phase to goes at the top.

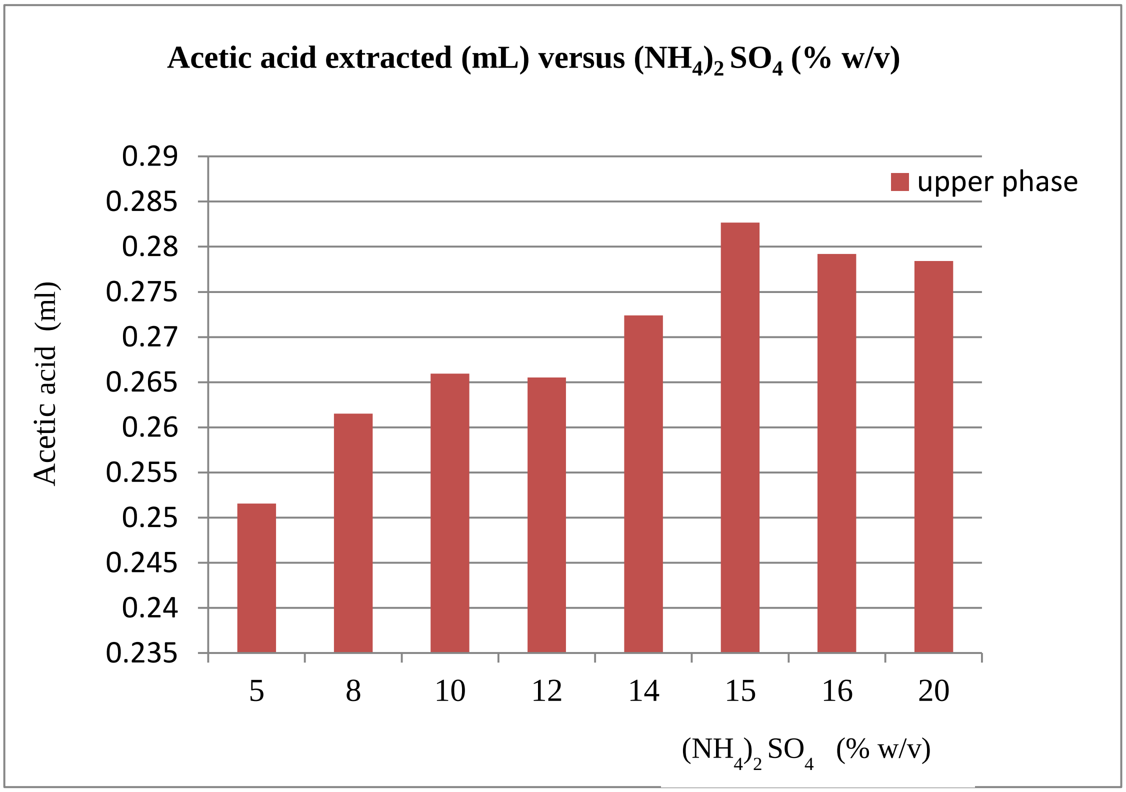


Figure 4.6: Acetic acid extracted at upper phase (mL) versus $(NH_4)_2SO_4$ (%w/v)

Yield is calculated to determine the amount of acetic acid recovered based on the original bio-oil. Based on the result, as the salt concentration increased, yield recovered of acetic acid is also increased. The highest yield is obtained at 15 % w/v of aqueous $(NH_4)_2SO_4$ with 28.27 % recovery of acetic acid. This clearly shows that, the amount of acetic acid recovered is depending on the dosage of salt added. Different concentration of salt gives different value of yield of acetic acid. Similar study is also conducted by Sukhbaatar et al. (2009) on the removal of acetic acid from bio-oil using calcium oxide. The study reveals that only 8.52% acetic acid managed to be removal as compared to

10.92% in raw bio-oil. Comparing the result obtained with the other studies done, there is a need for improvement in this study in order to maximize the recovery of acetic acid from bio-oil. Table 4.4 summarizes the yield of acetic acid according to the concentration of aqueous $(NH_4)_2SO_4$ added.

Table 4.5: Yield of acetic acid based on the concentration of aqueous $(NH_4)_2SO_4$

$(NH_4)_2SO_4$ (% w/v)	Yield (%)
5	25.15604
8	26.15274
10	26.59524
12	26.55352
14	27.24115
15	28.2678
16	27.9207
20	27.8424

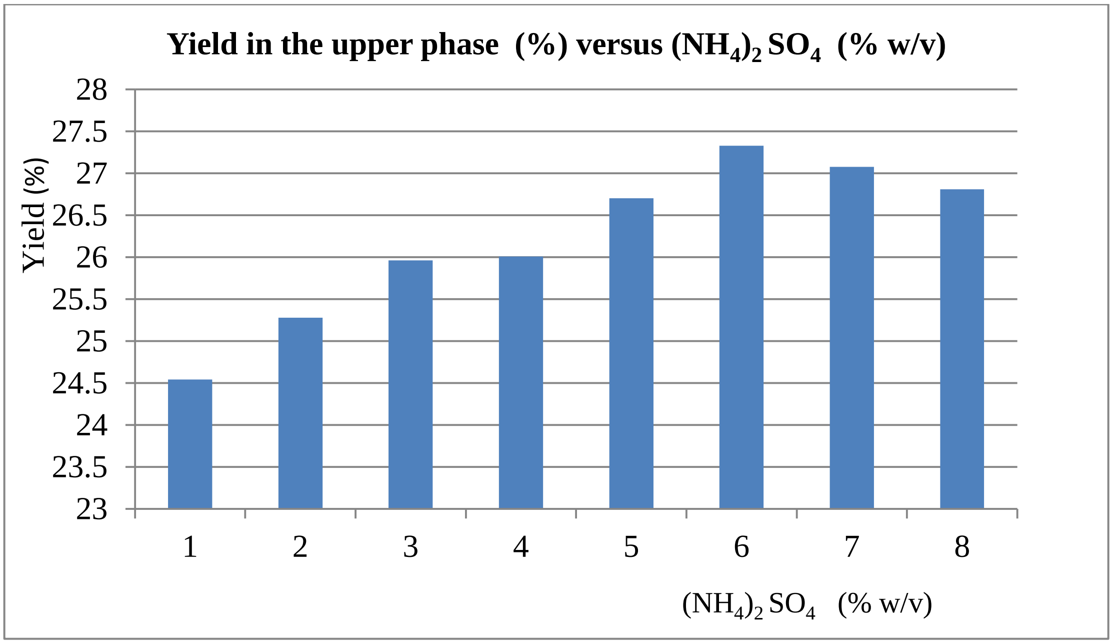


Figure 4.7: Yield in the upper phase versus concentration of aqueous $(NH_4)_2SO_4$

The extraction performance is also measured through distribution coefficient, K_D between upper layer and bottom layer. The ratio is obtained by dividing the amount of acetic acid extracted at the upper layer over the bottom layer. For the extraction process, a high K_D value is desirable in which the value is greater than 1. The reason is as K_D value is high, it shows that higher amount of acetic acid is extracted at the upper phase. However, in this experiment, K_D value calculated for each concentration of aqueous $(NH_4)_2SO_4$ shows that overall K_D value is lower than 1. It means that the amount of acetic acid is lower at the upper phase compared to the bottom phase. This is because only a small amount of acetic acid managed to be extracted through addition of salt. Overall, the highest K_D value is obtained at 15 % w/v of $(NH_4)_2SO_4$ with ratio of 0.38. The lowest extraction performance is obtained at 5 % w/v of $(NH_4)_2SO_4$. This indicates that lower concentration of $(NH_4)_2SO_4$ leads to low amount of acetic acid extracted at the upper phase. Table 4.5 summarized the overall K_D with respect to the concentration of aqueous $(NH_4)_2SO_4$.

Table 4.6: Distribution coefficient, K_D with respect to the concentration of aqueous $(NH_4)_2 SO_4$

$(NH_4)_2 SO_4$ (% w/v)	Distribution coefficient, KD
5	0.325274
8	0.338326
10	0.350652
12	0.351501
14	0.364292
15	0.376058
16	0.371325
20	0.366286

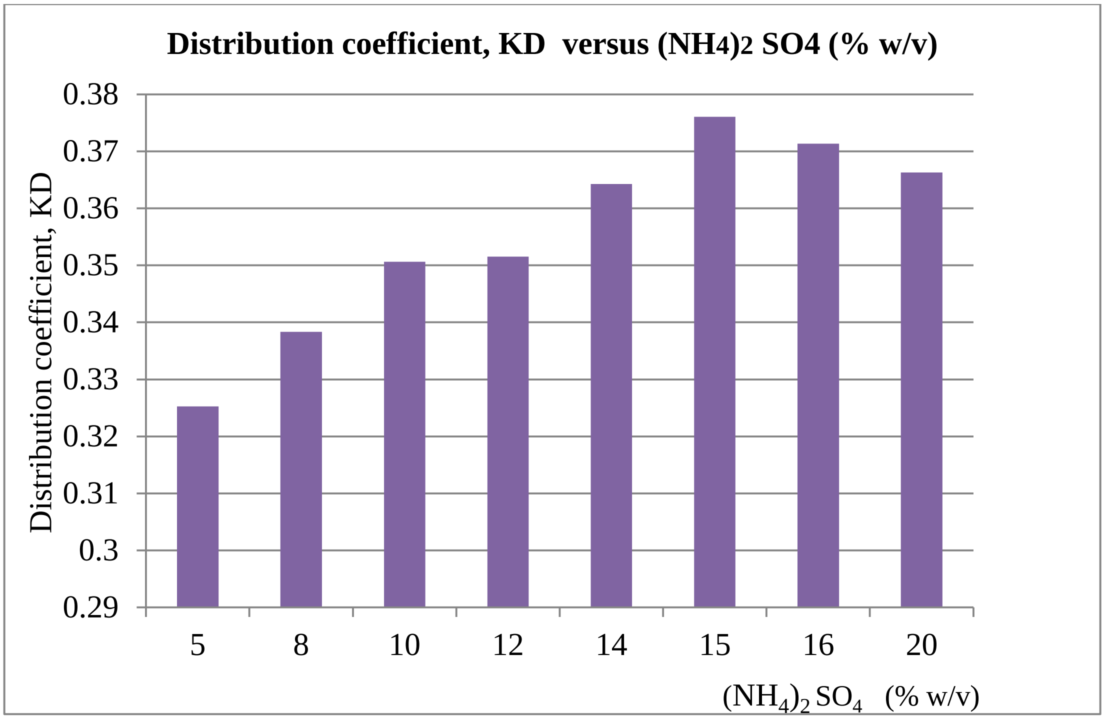


Figure 4.8: Distribution coefficient, KD versus concentration of aqueous $(NH_4)_2SO_4$

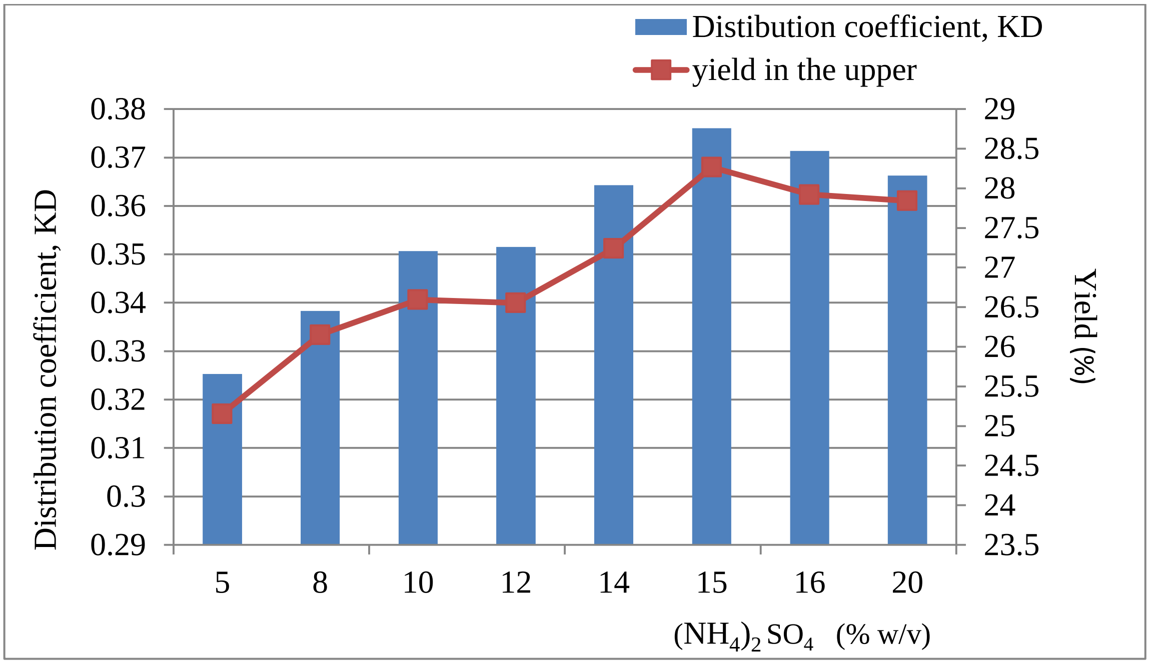


Figure 4.9: Distribution coefficient, KD and yield in the upper versus concentration of aqueous $(NH_4)_2SO_4$

Figure 4.8 shows yield and distribution coefficient of acetic acid in 5 to 20 % w/v of aqueous $(NH_4)_2 SO_4$. The graph clearly shows the highest value is obtained at 15 % w/v of aqueous $(NH_4)_2 SO_4$. Meanwhile, the lowest recovery of acetic acid is at 5 % aqueous $(NH_4)_2 SO_4$. Thus, it can be concluded that the optimum concentration of aqueous $(NH_4)_2 SO_4$ is at 15 % w/v of aqueous $(NH_4)_2 SO_4$ with yield of 28.27% and K_D value of 0.38 Table 4.6 summarized the findings.

Table 4.7 Yield and distribution coefficient, K_D of 8 % w/v of aqueous $(NH_4)_2 SO_4$

$(NH_4)_2 SO_4$ (% w/v)	Yield	Distribution coefficient, KD
15	28.27	0.38

CHAPTER 5

CONCLUSION

In conclusion, the extraction of acetic acid from bio-oil can be conducted by using aqueous salt system. Several procedures need to be carried out at first such as to prepare the synthetic bio-oil and characterize acetic acid amount in the bio-oil. In addition, the study conducted shows that with addition of 1ml aqueous $(NH_4)_2SO_4$ in 10 ml of bio-oil resulted in phase separation of bio-oil with 24-28 volume % at the top phase and 72-78 volume % at the bottom phase . Optimum concentration is obtained at 15 % w/v of aqueous $(NH_4)_2SO_4$ with yield of 28.27 % of acetic acid.

Future research will be focused on the optimizing the phase separation, type and concentration of salt solution so that it can expand into larger scale. As the upper and bottom layer of bio-oil contained different compound, effective separation of both phase will result in better yield. The compound which contains in both layers can be turned into value added chemical such as acetic acid and phenol.

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APPENDICES

Appendix

Table 1: Main properties of original bio-oil (Xu et al., 2008)

Properties	Bio-oil
Water content	33%
pH	2.82
Calorific value (kJg-1)	14.3
Density (gcm-3)	1.16
Dynamic viscosity at 303K	10.5

Table 2: Mass ratio, water contents, calorific value for two phase separation of bio-oil B (Qin et al., 2009)

Reagent added	Mass ratio	Density		Water (%)		HV (MJ/kg)	
	U:B	U	B	U	B	U	B
H2O	95:5	1.15	1.22	39.7	18.6	12.8	23.0
Li Cl	64:36	1.18	1.25	41.8	16.3	11.2	28.0
CaCl2	74:26	1.13	1.23	42.0	17.8	12.4	23.8
(NH4)2SO4	78:22	1.16	1.23	40.1	19.0	12.5	23.3