

Conversion of Bio Oil to Biodiesel Using Adsorptive Distillation Approach

by

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

DECEMBER 2010

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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,

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December 2010

CERTIFICATION OF ORIGINALITY

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

NADIAH BINTI JAMIL

ABSTRACT

This purpose of this project is to find a suitable method for conversion of bio oil to biodiesel through adsorptive distillation approach. This is to satisfy the need in finding latest technological advancements of the production of biodiesel. The problem needed to be assessed is whether the approach of adsorptive distillation is feasible for the conversion of bio oil to biodiesel.

There have been many efforts to produce biodiesel in many methods as this fuel can be used in standard diesel engines. Most methods of converting biodiesel use transesterification process. The technology of converting bio oil to biodiesel using the adsorptive distillation approach is still new and is rarely used as a conversion process.

The method for conversion uses the rotary evaporator. The bio oil will be reacted with an alcohol, in this case propanol. Sulphuric acid will be used as a catalyst in the reaction. At the same time, water will be adsorbed by the molecular sieves to force the reaction to the right side.

In conclusion, it is hoped that this project can prove that this method is feasible in converting bio oil to biodiesel and can be used in the future for the production of biodiesel.

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor, Associate Professor Dr. Suzana Yusup, for guiding and giving motivation to work on this Final Year Project I (FYP 1). Without her contribution, I would not have managed to gain this much knowledge on the project.

My sincerest appreciation goes to Mr. Wissam, the research officer also working on this project. He has helped me a lot in terms of the research methods and the literatures related on the project.

I would also like to thank my internal examiner, Professor Yoshimitsu Uemura for also helping me out on the project. Without his views and advice, I would have not gotten a clear picture on the project like I have now.

Finally, I would like to thank all my friends at Universiti Teknologi PETRONAS (UTP) especially my coursemates for giving me the moral support for the past weeks and also sharing their knowledge with me.

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CHAPTER 1

INTRODUCTION

1.1 Background

The world is currently facing fuel shortage due the diminishing natural resources. This has led to the increase interest in the technological developments of alternative fuel sources such as bio-fuels. Besides diminishing resources, the undesirable environmental impact of using fossil fuels is also one of the primary reasons for the increased interest in bio-fuels. This is because burning of fossil fuels produces among others, carbon dioxide which leads to an increase in greenhouse gas emissions. High petroleum prices and the need to spur rural development also have lead to the interest in these bio-fuels.

One of the main sources of alternative fuels is biodiesel. There have been many efforts to produce biodiesel in many methods as this fuel can be used in standard diesel engines. Biodiesels are methyl or ethyl esters of fatty acids with properties that are quite similar to those obtained for diesel derived from petroleum. Biodiesel is commonly derived from the transesterification of vegetable oils or animal fats with alcohols using acidic or basic catalysts. Biodiesel can be produced from various sources such as vegetable oils, biolipids, soybeans and algae oil. Bio oils can also be converted to biodiesel. However, the technology is still new and is rarely used as a conversion process.

Bio oil is produced from the pyrolysis of biomass. Biomass is biological material from living or recently living organisms. In the context of biomass for energy, this is most often referred to plant-based materials. However, it can be equally applied to both animal and vegetable derived material. Biomass offers huge potential in Malaysia because there are many sources of biomass waste such as palm-oil plantations, forestry wood products and sugar cane, cocoa and rubber cultivation. Energy from biomass can be derived by burning it but it can also be converted to

other forms of useable energy, like methanol or transportation gases such as ethanol and biodiesel.

As mentioned before, the pyrolysis of biomass can produce bio oils. The bio oil then can be upgraded to biodiesel using distillation methods. The pyrolysis technology is highly advanced. Pyrolysis is a process in which organic materials are chemically decomposed into simpler molecules by heat absence in oxygen. Temperature and residence time play an important roles for the yield. The liquid yield of pyrolysis is known as bio oil. This technology is able to convert up to 70% of the biomass into crude bio oil.

Bio oil, which is also known as biomass pyrolysis liquids, pyrolysis oils, or bio-crude oils are dark brown, water-miscible, free flowing liquids with an acrid or smoky odour which comprises of highly oxygenated compounds and water. A large variety of applications for bio oil have been proposed, which includes the use as fuel in boiler systems, stationary diesel engines, gas turbines, and Sterling engines. However due to certain of its characteristics such as poor vitality and high viscosity, the bio oil has to be further upgraded to improve its properties so that the fuel can be used efficiently. The upgrading of bio oil can produce biodiesel.

Various methods of the production of biodiesel from bio oil are done by reactive distillation and adsorptive distillation methods. For this research, the adsorptive distillation method of upgrading bio oil to biodiesel is studied. In an adsorption process, one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent, and so the separation process is complete. Here, the main reason adsorptive distillation is used is to remove the excessive water content in the bio oil. The removal of water is essential to drive the equilibria to the product side.

Molecular sieves are used as the adsorbents to capture the water for the adsorption process. Molecular sieves contain tiny pores that have a precise and uniform size. They are used as adsorbents for gases and liquids. They often function as a desiccant, which is a hygroscopic substance that induces a state of dryness in its surrounding areas.

Distillation is a method of separating mixtures based on differences in their volatilities in a boiling liquid mixture. Distillation is a unit operation, or a physical separation process, and not a chemical reaction. For this project, adsorptive distillation method is used. The rotary evaporator equipment will represent the distillation part while molecular sieves used will represent the adsorptive part.

1.2 Problem Statement

Alternative fuel technologies are the current focus in the oil and gas industry due to diminishing natural fuel sources in the world. This will affect the economy a lot as every sector is dependent on fuel, thus the need to find methods to produce various types of alternative fuels.

Biodiesel is one of the common alternative fuels. The main advantage of biodiesel is that it can be used in standard diesel engines, without the need of modifying the engine to support the fuel. There are a few ways to produce biodiesel but the method in focus here is the new method in converting bio oil to biodiesel using adsorptive distillation approach.

However, since the technology of converting of bio oil to biodiesel using adsorptive distillation is quite new, the problem is to prove whether it is feasible to use this method for biodiesel production. This method of conversion must be compared with other current methods to see if this method can yield more of the biodiesel compared to the current methods.

1.3 Objectives of Project, Scope of Study And Outline of Report:

By taking into account all the limitations for this research project, the objectives of this research are:

- i. To investigate the properties and characteristics of bio oil to find a suitable conversion method to biodiesel
- ii. To validate whether bio oil can be converted to biodiesel using the adsorptive distillation approach
- iii. To apply the best method for the conversion of bio oil to biodiesel using adsorptive distillation

The scope of this project is to determine the most suitable method in converting bio oil to biodiesel using the adsorptive distillation approach. A modified rotary evaporator will be used to extract the upgraded bio oil. Molecular sieves in forms of tea bags will be used as adsorbents in the experiment to remove the water content in the bio oil. The upgraded bio oil properties and characteristics will be tested using the gas chromatography and thin layer chromatography. Various methods will also be compared so that the best approach can be chosen to convert the bio oil to biodiesel. This is because this is still a new technology to produce biodiesel.

In Chapter 2, the literature work is done to have a complete understanding about the aims of this research project. A strong knowledge about the basic fundamentals of biomass, bio oil, biodiesel and the method of adsorption can help to build a strong understanding to achieve the objectives of this research project.

In Chapter 3, the methodology of the experiments is described. The method is obtained by referring to journals and discussion with supervisors. Since this is a new method, many experiments have to be done to find the most feasible method in using the adsorptive distillation approach.

In Chapter 4, the work progress is discussed. The current update on the project is looked into and future works to be done is also mentioned.

CHAPTER 2

LITERATURE REVIEW

2.1 Bio Oil

Bio oils are produced from the pyrolysis of biomass. They are dark brown, water miscible, free flowing liquids, with an acrid or smoky odour. They are complex mixtures of compounds derived from the rapidly and simultaneously depolymerising of cellulose, hemicelluloses and lignin with a rapid increase in temperature. They comprise of highly oxygenated compounds and water. Chemically, they have high water content, more or less solid particles and hundreds of organic compounds with a complex mixture [1-2].

Bio oil comprises of a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics. Bio oil contains many reactive species which contribute to unusual attributes [3]. The following points will discuss the properties of bio oil in more detail.

2.1.1 Water Content

The water content is usually high, with a range of 15-30%, as water is the most abundant single component in the bio oil. This results from the original moisture in the feedstocks and dehydration reactions during the fast pyrolysis process. The content of the water is determined by Karl-Fischer titration [1].

Water is hard to be removed from bio oils. The presence of water has both positive and negative effects on the storage and utilization of bio oils. The high water content, however, decreases the specific heating value and may cause phase separation of bio oils [1]. Moreover, it increases ignition delay and reduces

combustion rates and adiabatic flame temperatures during the combustion process. On the other hand; it helps to reduce the viscosity of the bio oil.

Table 3
Composition of bio-oil determined by GC/MS (mass % of bio-oil).

No	Compound	RT (min)	Oil mallee	Pine pellets
1	Hydroxyacetaldehyde	1.6	3,71	–
2	Acetic acid	1.9	5.73	2.66
3	Propane, 2,2 dimethoxy	2.1	0.59	0.52
4	2-propanone, 1-hydroxy	2.3	2.16	3.55
5	Propanoic acid	3.2	1.82	2.54
6	Cyclopentanone	4.7	0.12	0.16
7	2-Furaldehyde	5.9	0.33	0.41
8	Furfuryl alcohol	7.0	0.02	0.03
9	Furan, tetrahydro-2,5-dimethoxy (<i>cis</i>)	7.8	0.34	0.22
10	Furan, tetrahydro-2,5-dimethoxy (<i>trans</i>)	8.4	0.29	0.18
11	2 (5H)-Furanone	9.2	0.03	0.04
12	2 (3H)-Furanone, 5-methyl	9.7	0.07	0.05
13	2-Furanethanol, beta-methoxy	11.2	0.70	0.57
14	Phenol	13.2	0.57	0.32
15	1,2-cyclopentanedione, 3-methyl	14.7	0.04	0.01
16	Phenol 2-methyl	16.1	0.05	0.03
17	Phenol 3-methyl (<i>o</i> -cresol)	16.4	0.02	–
18	Phenol, 2-methoxy (guaiacol)	17.6	0.12	0.368
19	2(3H) Furanone, dihydro-3-hydroxy-4, 4-dimethyl	19.0	0.07	0.04
20	Phenol, 2-methoxy-4-methyl	22.5	0.05	0.39
21	Eugenol	29.8	0.51	0.21
22	Vanillin	33.7	1.46	1.15
23	1,6 anhydro-beta-D-glucopyranose	35.4	6.49	6.32
24	Hydroquinone	36.9	0.09	–
25	Stilbene	38.4	0.12	–
26	Phenol, 2,6 dimethoxy-4-(2-propenyl) (<i>cis</i>) (4-propenyl syringol)	39.8	0.56	–
27	Phenol, 2,6 dimethoxy-4-(2-propenyl) (<i>trans</i>) (4-propenylsyringol)	41.6	0.41	–
28	Syringaldehyde (benzaldehyde, 4-hydroxy-3,5 dimethoxy)	42.0	1.16	–
29	Propanoic acid, 3-(4-hydroxy-3-methoxyphenyl)-	43.4	0.99	–
30	2,5-dimethoxy-4-ethylbenzaldehyde	43.6	0.31	–
31	Dibenzothiophene	44.6	0.17	0.05

Table 1.1: Composition of Bio Oil determined by GC/MS (mass percent of bio oil)

2.1.2 Heating Value

The lower heating value (LHV) of bio oils is typically 14-18 MJ/kg which is much lower than that of petroleum fuels that have a LHV of 43 MJ/kg. This is attributed to the high oxygen content of bio oils [1]. Bio oils are usually directly measured for their high heating values (HHV). Thus, the LHV can be calculated by the following equation proposed by Oasamaa et. al:

$$\text{LHV} = \text{HHV} - 218.3 \times H\% \text{ (wt\%)} \text{ (KJ/kg)} [1]$$

2.1.3 Viscosity

Bio oils have high viscosities thus creating problems with atomization and smooth combustion in fuel applications. This will make filtration and distillation difficult for the bio oil. Generally, viscosities of bio oils vary in a wide range (10-100 cP at 40°C). Moderate preheating of bio oils is useful to reduce their viscosities and facilitate pumping and atomization. However, at temperatures higher than 80°C, the whole properties of bio oils will be totally altered as a result of accelerated ageing reactions [1].

2.1.4 Thermal stability of bio oils

Bio oils are chemically unstable as viscosity and molecular weight increases at the same time water content increases. Ageing process also accelerates with increases in temperature. Four stages can be observed during heating of bio oils: thickening, phase separation, gummy formation from the pyrolytic lignins (at around 140°C) and char or coke formation from the gummy phase at higher temperatures.

Boucher et. al. treated a bio oil sample at 50°C and 80°C. He found that the bio oil properties kept at 80°C were significantly altered, while there no significant changes for the oil kept at 50°C for a week [1].

2.1.5 Atomization property

Atomization property is the process of breaking liquid into small droplets for spray combustion. Various ways have been developed to generate sprays with the basic principle of a high relative velocity between the liquid and the surrounding air. In regard to liquid properties, viscosity and surface tension are the most important parameters. The viscosity and surface tension of bio oils are higher than those of light petroleum fuels. Thus, favourable atomization of bio oils requires strict conditions [1].

2.2 Biodiesel

2.2.1 Overview on Biodiesel

Biodiesel is a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils or animal fats [5]. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulphur and aromatics [6].

2.2.2 Biodiesel Production

Biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. Soybean oil and methanol are the most popular feedstocks in the United States [6]. Soybeans are a major U.S. crop and government subsidies are available to make the fuel economically attractive to consumers who need or want to use a nonpetroleum-based fuel. Biodiesel from soybeans is sometimes called soydiesel, methyl soyate, or soy methyl esters (SME). In Europe, most biodiesel is made from rapeseed oil and methanol and it is known as rapeseed methyl esters (RME). The University of Idaho has done considerable work with rapeseed esters using ethanol, which produces rapeseed ethyl esters (REE).

Biodiesel can also be made from other feedstocks [5]:

1. Other vegetable oils such as corn oil, canola (an edible variety of rapeseed) oil, cottonseed oil, mustard oil, palm oil, etc.
2. Restaurant waste oils such as frying oils
3. Animal fats such as beef tallow or pork lard
4. Trap grease (from restaurant grease traps), float grease (from waste water treatment plants), etc

The process leaves behind two products -- methyl esters (the chemical name for biodiesel) and glycerin (a valuable byproduct usually sold to be used in soaps and other products).

The basic routes to biodiesel production from oils and fat are [7]:

- Base catalyzed transesterification of the oil with alcohol.
- Direct acid catalyzed esterification of the oil with methanol.
- Conversion of the oil to fatty acids, and then to Alkyl esters with acid catalysis.

2.2.3 Biodiesel Emissions

Biodiesel is the first and only alternative fuel to have a complete evaluation of emission results and potential health effects submitted to the U.S. Environmental Protection Agency (EPA) under the Clean Air Act Section 211(b). The data gathered complete the most thorough inventory of the environmental and human health effects attributes that current technology will allow. The table shows the biodiesel emission [8].

Emission Type	B100	B20
Regulated Total Unburned Hydrocarbons	-67%	-20%

Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
Nox	+10%	+2% to -2%
Non-Regulated		
Sulfates	-100%	-20%*
PAH (Polycyclic Aromatic Hydrocarbons)**	-80%	-13%
nPAH (nitrated PAH's)** -	-90%	50%***
Ozone potential of speciated HC	-50%	-10%

* Estimated from B100 result

** Average reduction across all compounds measured

*** 2-nitroflourine results were within test method variability

Table 1.2: Biodiesel Emissions

Criteria pollutants are reduced with biodiesel use. Tests show the use of biodiesel in diesel engines results in substantial reductions of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides stay the same or are slightly increased.⁸

- Sulphur emissions are essentially eliminated with pure biodiesel. The exhaust emissions of sulphur oxides and sulphates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel.

- The ozone (smog) forming potential of biodiesel hydrocarbons is less than diesel fuel. The ozone forming potential of the hydrocarbon emissions is 50 percent less than that measured for diesel fuel.
- Carbon Monoxide -- The exhaust emissions of carbon monoxide (a poisonous gas) from biodiesel are on average 48 percent lower than carbon monoxide emissions from diesel.
- Particulate Matter -- Breathing particulate has been shown to be a human health hazard. The exhaust emissions of particulate matter from biodiesel are about 47 percent lower than overall particulate matter emissions from diesel.
- Hydrocarbons -- The exhaust emissions of total hydrocarbons (a contributing factor in the localized formation of smog and ozone) are on average 67 percent lower for biodiesel than diesel fuel.
- Nitrogen Oxides -- NO_x emissions from biodiesel increase or decrease depending on the engine family and testing procedures. NO_x emissions (a contributing factor in the localized formation of smog and ozone) from pure (100%) biodiesel increase on average by 10 percent.

2.2.4 Applications and usage

Alternatively this fuel can also be blended in any proportion with diesel in the diesel engines of modern automobiles. However gaskets and hoses made with natural rubber as found in automobiles made up to the early nineties tend to be degraded more by biodiesel than by petro-diesel because of certain solvent properties of biodiesel. Modern engines however use FKM in place of rubber as it does not react with biodiesel. The transition from petro-diesel to biodiesel may be made gradually since the latter is often found to disintegrate the residual petro-diesel deposit on the fuel tanks resulting in clogging of the fuel filters. A blend of the two types of fuels in appropriate proportions should be resorted to before switching over fully to biodiesel to reduce this possibility. A better option while using biodiesel is to replace the fuel filters on the auto engines and heaters [9].

2.2.5 Benefits of Biodiesel

There are many benefits of the usage of biodiesel. Biodiesel is renewable and contributes less to global warming than fossil fuels due to its closed carbon cycle. Because the primary feedstock for biodiesel is a biologically-based oil or fat, which can be grown season after season, biodiesel is renewable. And, since most of the carbon in the fuel was originally removed from the air by plants, there is very little net increase in carbon dioxide levels. However, some fossil carbon is contained in the methanol used to make methyl esters, and some fossil fuel is used during the production process [5].

The exhaust emissions from biodiesel are lower than with regular diesel fuel. Biodiesel provides substantial reductions in carbon monoxide, unburned hydrocarbons, and particulate emissions from diesel engines. While the carbon monoxide and unburned hydrocarbons from diesels are already very low compared with gasoline engines, biodiesel reduces them further. Particulate emissions, especially the black soot portion, are greatly reduced with biodiesel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NO_x) emissions with biodiesel. This increase in NO_x can be eliminated with a small adjustment to the engine's injection timing while still retaining a particulate decrease [5].

Biodiesel has excellent lubricating properties. Even when added to regular diesel fuel in an amount equal to 1-2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel [5].

2.3 Adsorbents

Adsorbents are a substance, usually porous in nature and with a large surface area that can adsorb substances onto its surface by intermolecular forces. The adsorbents used for this project is molecular sieves. Molecular sieves are used to dehydrate the solvents used in the final stages of dehydration and embedding [10].

Molecular sieves are typically zeolite compounds that strongly adsorb water and have carefully controlled pore sizes [11]. While both the solvent and the water

will adsorb strongly to the molecular sieve surfaces, the large surface area within the pores is only accessible to the smaller water molecules, so they are effectively removed from the solvent. It is different from the common filter as it operates at a molecular level. For example (refer to Appendices I), water (of size 1.93Å) will enter that 3Å pore size while acetone (of size 3.08Å) will largely be excluded [8]. Water will be able to occupy the large surface area inside the pores and thus be removed. If the solvent could also enter the pores, it would compete with water for the surface area and there would be little or no removal of the water from the bulk solvent [11].

The pores also act as a trap for the penetrating water molecules which are retained within the pores. Because of this, they often function as a desiccant. A molecular sieve can absorb water up to 22% of its own weight. The principle of absorption to molecular sieve particles is somehow similar to that of size exclusion chromatography [11].

2.4 Reactions

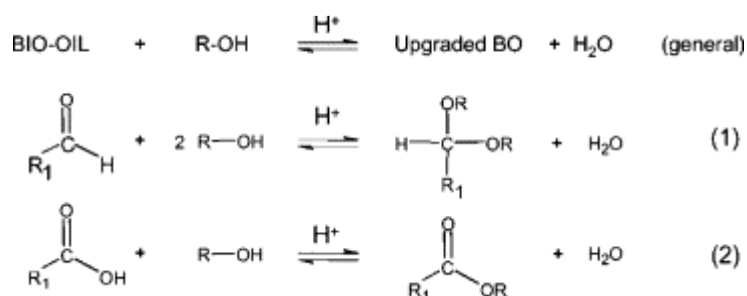


Figure 1.1: Reactions between bio oil components and alcohol

The reactions occur in the bio oil conversion to biodiesel is acetalization and esterification. The bio oil will be reacted with an alcohol, or in this project, with propanol. In (1), aldehydes in the bio oil will be reacted with the alcohol, while in (2) shows the reaction between the organic acid in the bio oil that will produce free acid methyl ester or monoalkyl esters, where they are the main components of biodiesel [4].

2.5 Alcohol Screening

To convert the bio oil to biodiesel, alcohol is needed. This is because when alcohol is added; viscosity of the bio oil is substantially reduced, which facilitates the pumping and atomization of these oils in combustion apparatus. It also improves the filterability which could be relevant for removing cation contaminants [4].

The alcohol used for this reaction is propanol. For adsorptive distillation, a lower boiling point of alcohol is used. It has to have a lower boiling point than water as an alcohol of higher boiling point will vaporize the water content in the bio oil. Table 1.1 compares the difference of the use of alcohol between adsorptive and reactive distillation [4].

Process	Reactive adsorption using Molecular Sieve (Radlein, 1996)	Reactive distillation using high boiling alcohol
Alcohol	Low b.p. (<373 K): ethanol, propanol, etc.	High b.p. (>383 K). Butanol, ethylene glycol, etc.
Processing aid	<i>Molecular sieves</i> , relatively large amount per BO used	<i>Catalyst</i> , relatively small amount per BO used
Conditions	293–343 K, atmospheric	293–343 K, reduced pressure

Table 1.3: Comparison of BO upgrading methods by alcohol treatment: reactive adsorption and reactive distillation.

2.6 Catalyst Screening

For the catalyst screening, sulphuric acid, potassium hydroxide (KOH), and Nafion SAC 13 are tested. Referring to Table 1.2 below, when using KOH, significant amounts of water were produced by chemical reactions. However this was much lower than a reaction where no catalyst was used. The pH of the product using KOH was still slightly acidic. It implies that the amount of added KOH is insufficient to neutralize all the organic acids present in the bio oil. Hence, instead of creating a basic environment, the experiments were still performed under acidic conditions. Therefore, the water produced by chemical reactions likely originates from acid catalyzed esterification and acetalization reactions [4].

Catalyst	ΔW_R , wt%	Product pH
H ₂ SO ₄ (96%)	23.9	0.5
no cat.	6	3.1
KOH	4	5.5

Table 1.4: Results for reactive distillation experiment with n-butanol

To prevent a subsequent neutralization step, solid catalysts were used. Solid catalysts have been widely used to catalyse esterifications and other liquid phase acid catalysed reactions. For initial screening studies, Nafion SAC 13 was selected to overcome the low product pH and catalyst recycle-ability problem using homogenous acids like sulphuric acids. The results using 1.6 wt% of catalyst (on bio oil-n-butanol) is presented in the Figure 1.2 [4].

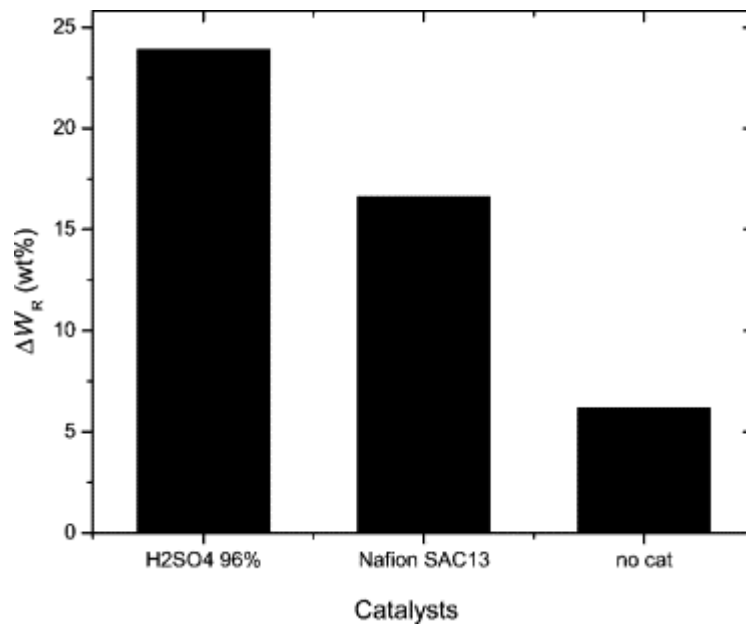


Figure 1.2: Catalysts performance (ΔW_R) for H₂SO₄ and Nafion SAC 13.

Conditions: $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

The performance for Nafion SAC 13 was lower than for sulphuric acid. Apparently, the catalytic effect of Nafion SAC 13 on the esterification and acetalization reactions depicted in Figure 1.2 is less than sulphuric acid. However, there is a clear catalytic effect of Nafion as the amount of water produced is higher than for the blank without catalyst addition [4].

Although the performance of Nafion is lower compared to sulphuric acid, the pH of the product is significantly higher (pH = 3.2 versus 0.5 for sulphuric acid). The pH of the product using Nafion is slightly higher than the starting bio oil, implying that conversion of the organic acids in the BO matrix is still far from quantitative. In conclusion, these screening studies indicate that solid acid catalysts have high potential for the reactive distillation concept, although optimization studies are required to achieve further reductions in product acidity and water content[4].

2.7 Method of Upgrading of Bio Oil to Biodiesel

By chemically and thermally stabilizing the products, it prevents the bio oils from aging and thus avoiding problems of viscosity increasing with time and the deposition in fuel lines. Besides that, the specific heating value of the bio oil can be enhanced by combination with a suitable alcohol and further by reducing the water content. A method of upgrading bio oils to chemically and thermally stabilized products includes the following steps [12]:

- (1) Adding alcohol to liquid products obtained from pyrolysis process (bio oil).
- (2) Mixing the alcohol and liquid products.
- (3) Removing the water without removing alcohol, thereby increasing the specific heat value and lowering acidity and viscosity.

For this project, the distillation part is represented by the rotary evaporator and the molecular sieves will act as the adsorptive part of the process.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

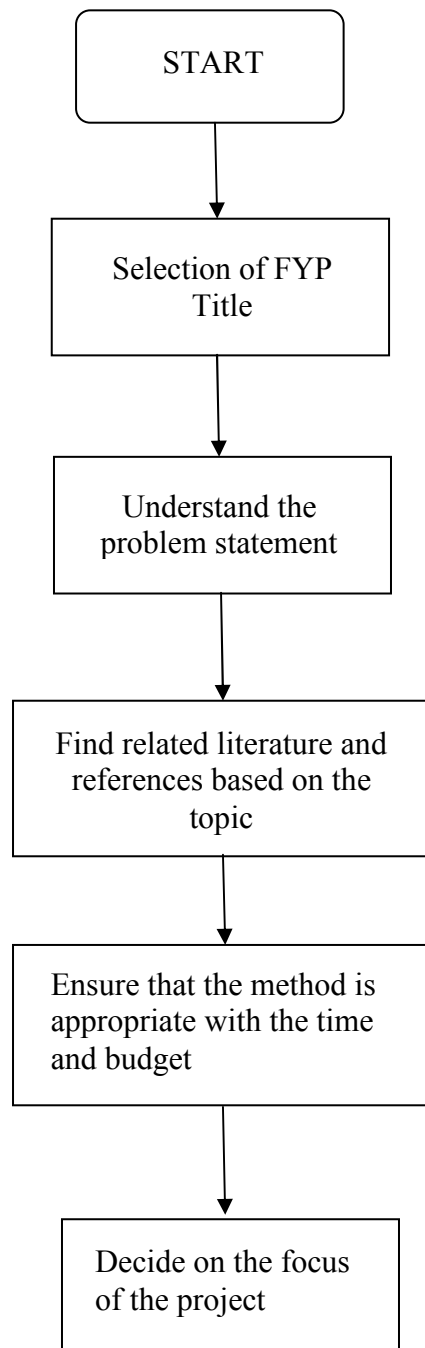


Figure 1.3: Research Methodology for the Project

3.2 Gantt Chart

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continue														
2	Submission of Progress Report 1														
3	Project Work Continue														
4	Submission of Progress Report 2														
5	Project work continue														
6	Poster Exhibition														
7	Submission of Dissertation (soft bound)														
8	Oral Presentation														
9	Submission of Project Dissertation (Hard Bound)														

 Process
 Suggested Milestone

Table 1.5: Gantt Chart and Milestones for the Project

3.3 Effects of Vapour Pressure and Temperature Experiment

3.3.1 Objectives

To analyse the effects of vapour pressure and temperature and whether it complies with the Antoine Equation

3.3.2 Apparatus and Equipments

The equipment used is rotary evaporator. It is connected with vacuum pump. Both of the equipments will be placed in a fumehood to ensure that the fumes or smell from the experiment is contained. Parts of the rotary evaporator are:

1. Condenser
2. Reactant Flask
3. Product Flask
4. Water Bath
5. Temperature Controller
6. Vacuum Pump
7. Pressure Controller

The function of the vacuum pump is to reduce the pressure so that the boiling point of the component can be reduced.

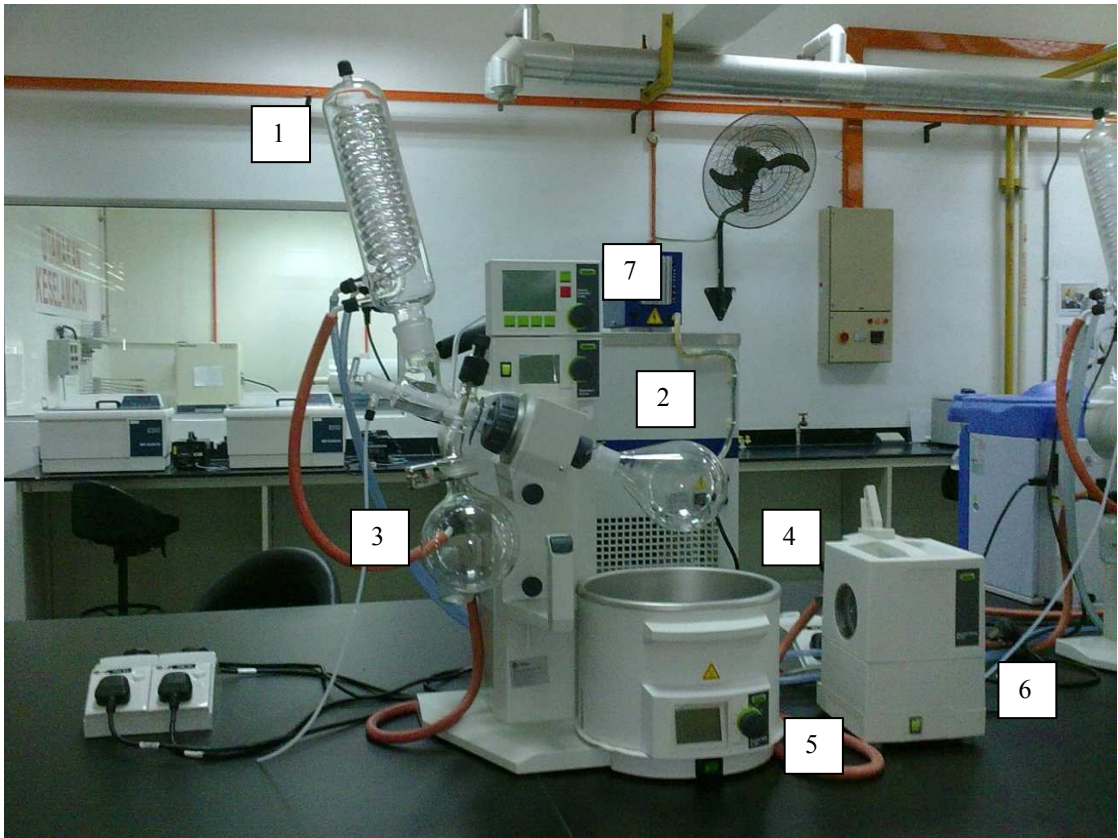


Figure 1.4: Rotary Evaporator



Figure 1.5: Fume hood



Figure 1.6: New Fumehood

3.3.3 Chemicals

The materials used for this experiment are acetic acid acting as bio oil, propanol as the alcohol, sulphuric acid as the catalyst, and water as the heating medium in the rotary evaporator.

3.3.4 Process Methodology

Loading of Water Bath

1. Wash and dry the bath before use.
2. Fill the bath with distilled water.
3. Change the water only if there are contaminants.

Preparation of Bio Oil

Bio Oil for this experiment will be replaced by acetic acid as it is one of the main components of bio oil. It will be reacted together with alcohol and a catalyst, sulphuric acid.

Procedure

1. Switch ON the three power supplies.
2. Switch ON the equipments.
3. Press the handle down to immerse about $\frac{1}{4}$ of the flask in the water bath.
4. The experiment is 100% reflux, so ensure that the valve at product side is fully closed.
5. Set the following initial parameters as follows.

Maximum Temperature ($^{\circ}\text{C}$)	60
Pressure (m bar)	45
Rotation (rpm)	20

Table 1.6: Initial Parameters for Testing of Water

6. A mixture of bio oil and alcohol (propanol) are heated using a heating medium (e.g. water or oil).
7. The vapour will then be condensed in the condenser (at the top, referring to Figure 1.4).
8. The alcohol will be recycled, going back into the flask while the remaining of the mixture.

Shutdown

1. Reduce the temperature to 15°C .
2. Stop the pressure exerted from the vacuum pump.
3. Press the handle up to take out the immersed flask from the water bath.

Safety Measures

There are several safety measures that should be taken into account while running the experiment under the fumehood.

1. The blower should be kept on while the experiment is still running to ensure that there is air circulation in the fumehood.
2. The lights should be turn off to preserve electricity.

3. The lid of the fumehood should be kept closed at least $\frac{3}{4}$ of the fumehood to ensure that the any smell or fumes from the experiment are contained inside the fumehood.
4. The water outlet of the condenser should be properly drained so that no short circuit occurs if the water contacts with the electrical appliances.

3.4 Process Methodology for Neutralization Titration of Mixture Solution of Propanol and Acetic Acid Reaction Experiment

3.4.1 Objective

To determine either the reaction between propanol and acetic acid occurred or not by analysing the conversion of the reaction

3.4.2 Apparatus and Equipment

250 ml volumetric flask, 50 ml burette, 50 ml Erlenmeyer flask, condenser, 500 ml beaker, 250 ml flask, dropper, measuring cylinder.

3.4.3 Chemicals

Acetic Acid, Propanol, Phenolphthalein, NaOH

3.4.4 Procedure

A) Preparation of 1.0M of NaOH Solution

1. Weights 10g of NaOH pallet. (*refer Appendix III*)
2. Dissolve the pallet with distilled water in small beaker. Stir until all pallets are dissolved.
3. Pour the NaOH solution into 250ml volumetric flask. Add distilled water till the marked level.

B) Reaction of Propanol and Acetic Acid Mixture Solution.

1. Pour 140 ml of propanol into the 250 flask. (*refer Appendix IV*)
2. Add 10ml of acetic acid into propanol solution.
3. Collect 10ml of initial mixture sample for titration process.
4. Fill the 500ml beaker with tap water and put it on hot plate.
5. Set the temperature to ;

- i. 30°C (1st run)
 - ii. 40°C (2nd run)
 - iii. 50°C (3rd run)
6. Put the mixture flask inside the water bath (beaker)
 7. Collect 10ml of mixture sample every one hour for titration process.
 8. Run the experiment for 5 hours and get 5 sample of mixture solution.

C) Titration Process

1. Use the 1.0M of NaOH solution and fill it into the burette. Note down the volume of burette. (Take the initial mixture as reference)
2. Obtain 5ml of mixture sample.
3. Add few drops of phenolphthalein into the mixture. (mixture will remain colourless)
4. Place the mixture flask under the burette and start the titration process.
5. End the process when the colourless mixture changes to pink.
6. Note down the final burette volume.

3.5 Artificial Bio-oil Preparation

Based on GCMS result, the analysis shows that bio-oil is consisted with groups of carboxylic (26.54wt%), ketone (23.63wt%), phenol (16.98wt%), ester (7.17wt%), furan (6.31wt%), alcohol (5.55wt%), aldehydes (5.12wt%) and water (8.7wt%). By knowing the composition's percentage, preparation of artificial bio-oil will use:

No	Organic Group	Chemical	Wt%	Density (g/cm ³)
1	Carboxylic Acid	Acetic Acid	26.54	1.0490
2	Ketone	Ethyl Methyl Ketone	23.63	0.8050
3	Phenol	Phenol	16.98	1.0700
4	Ester	Methyl acetate	7.17	0.9320
5	Furan	Tetrahydro-Furan	6.31	0.8892
6	Alcohol	Methanol	5.55	0.7918

7	Aldehydes	2-Furaldehyde	5.12	1.1600
8	Water	Water	8.7	1.0000

Table 1.7: Composition Percentage of Bio Oil

Using this data of information, 100ml of artificial bio-oil will be made accordingly.

(Refer to Appendix V)

Organic Group	Chemical	Weight %	Density (g/cm ³)	Mass of 1ml	Mass fraction	Volume	Volume ratio	Volume used for 100ml mixture
Carboxylic Acid	Acetic Acid	26.54	1.0490	1.0490	2.0428	1.9474	0.2400	23.9959
Ketone	Ethyl Methyl Ketone	23.63	0.8050	0.8050	1.8188	2.2594	0.2784	27.8406
Phenol	Phenol	16.98	1.0700	1.0700	1.3070	1.2214	0.1505	15.0510
Ester	Methyl acetate	7.17	0.9320	0.9320	0.5519	0.5921	0.0730	7.2965
Furan	Tetrahydro-Furan	6.31	0.8892	0.8892	0.4857	0.5462	0.0673	6.7304
Alcohol	Methanol	5.55	0.7918	0.7918	0.4272	0.5395	0.0665	6.6480
Aldehydes	2-Furaldehyde	5.12	1.1600	1.1600	0.3941	0.3397	0.0419	4.1862
Water	Water	8.7	1.0000	1.0000	0.6696	0.6696	0.0825	8.2514
						<u>7.6970</u>	<u>8.1154</u>	<u>100</u>

Table 1.8: Volume Used for 100ml Mixture Bio Oil

In order to prepare 100ml of artificial bio-oil, we need 24ml of acetic acid, 27.8ml of ethyl methyl ketone, 15ml of phenol, 7.3ml of methyl acetate, 6.7ml of tetrahydrofuran, 6.6ml of methanol, 4.2ml of 2-furaldehyde and 8.3ml of distilled water.

3.6 Adsorptive Distillation Approach using Rotary Evaporator

3.6.1 Objectives

To take samples of the reaction between bio oil and alcohol to be analysed

3.6.2 Apparatus and Equipments

Refer to 3.3.2

3.6.3 Chemicals

Artificial Bio Oil (Refer to 3.5 for preparation method), Propanol, Sulphuric Acid, and Molecular Sieves 3A.

3.6.4 Procedure

Loading of Water Bath

1. Wash and dry the bath before use.
2. Fill the bath with distilled water.
3. Change the water only if there are contaminants.

Procedure

1. Switch ON the three power supplies.
2. Switch ON the equipments.
3. Insert the molecular sieves 3A in the condenser.
4. Press the handle down to immerse about $\frac{1}{4}$ of the flask in the water bath.
5. The experiment is 100% reflux, so ensure that the valve at product side is fully closed.
6. Set the following initial parameters as follows.

Maximum Temperature ($^{\circ}\text{C}$)	60
Pressure (m bar)	80
Rotation (rpm)	25

Table 1.9: Initial Parameters for Rotary Evaporator

7. Bio oil is mixed with catalyst sulphuric acid before being added together with propanol.
8. The flask is then heated until it has boiled according to the parameters set.
9. The sample is taken every 10 minutes.
10. After one hour, stop the experiment.

Shutdown

1. Reduce the temperature to 15°C .
2. Stop the pressure exerted from the vacuum pump.
3. Press the handle up to take out the immersed flask from the water bath.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effects of Vapour Pressure and Temperature on Water

An experimental run was done on water as the component to be tested. This experiment will follow Antoine Equation. Antoine Equation is a vapour pressure equation and describes the relationship between vapour pressure and temperature for pure components. Antoine Equation is given as:

$$\log_{10} p = A - \frac{B}{C + T}$$

Where, the water coefficients for the Antoine Equation are, $A = 8.07131$, $B = 1730.63$ and $C = 233.426$. The P-T curve obtained for water is shown in the figure below.

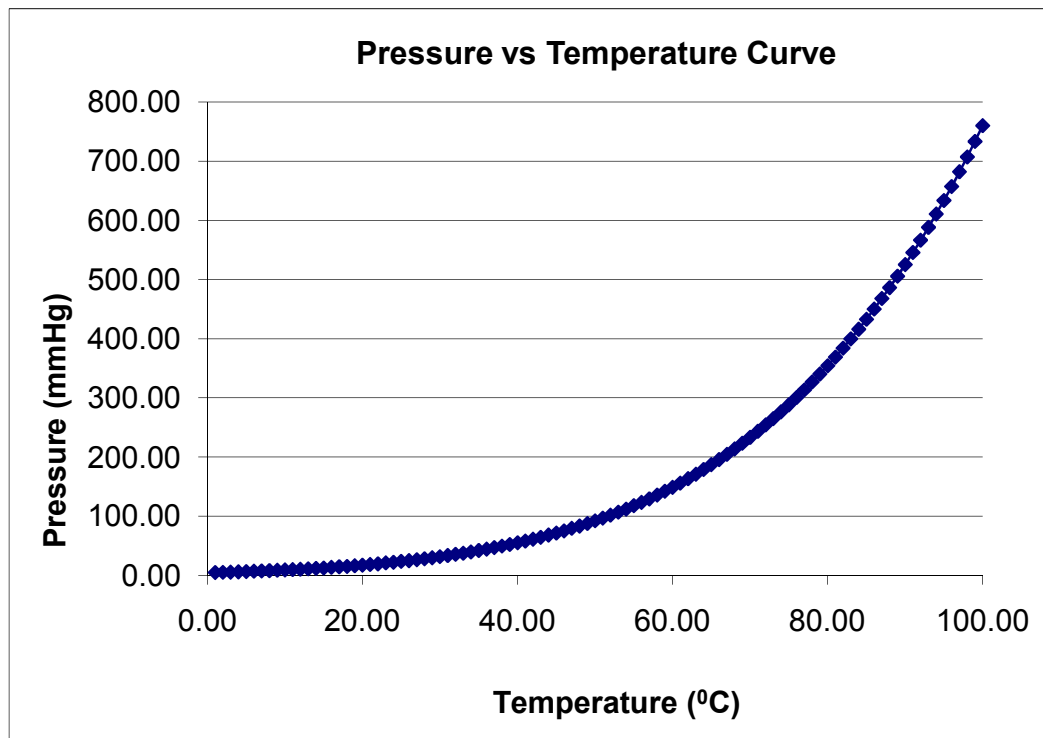


Figure 1.7: Pressure vs Temperature Curve for Water

From the experimental run on water, we can see that when the temperature of the water bath is set to a certain temperature, the vapour pressure of the water is similar

to what is obtained in the graph. Thus, this experiment complies with the Antoine Equation.

4.2 Effects of Vapour Pressure and Temperature on Propanol, Acetic Acid, and Mixture

The same equation from the previous experiment is used for this experiment. However, we will calculate the vapour pressure for pure components of propanol, acetic acid and the mixture of propanol and acetic acid.

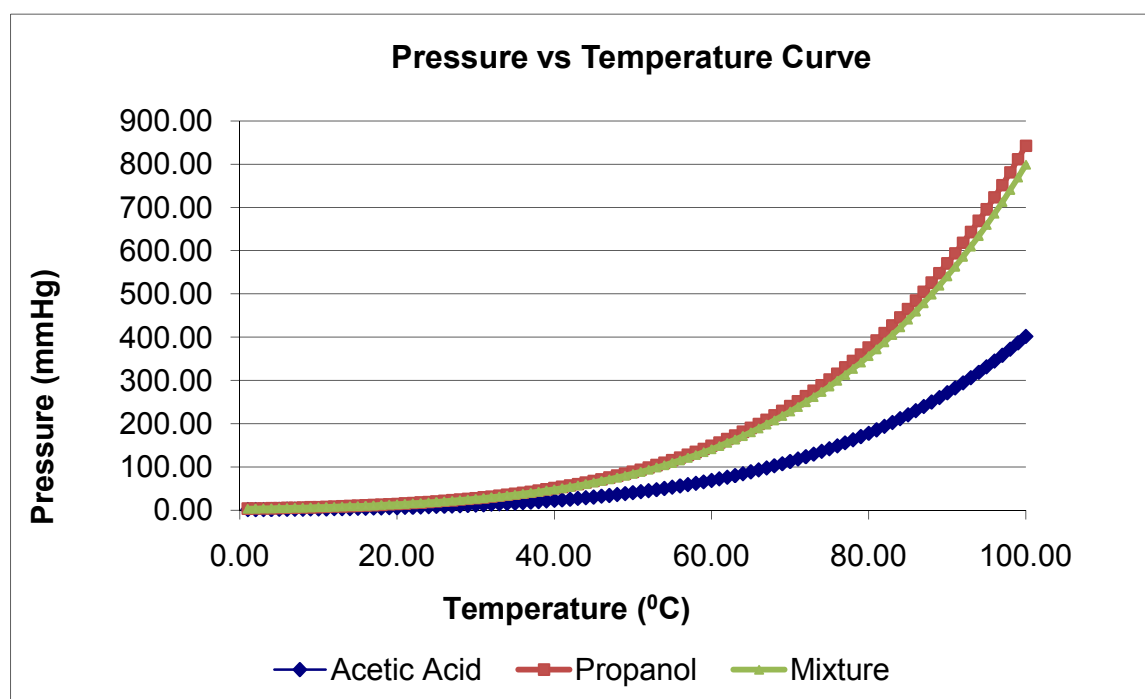


Figure 1.8: Pressure vs Temperature Curve for Acetic Acid, Propanol and Mixture

The same result can be seen for this experiment. When the temperature of the water bath is set to a certain temperature, the vapour pressure of the propanol is similar to what is obtained in the graph. The same case also happens for acetic acid and mixture of both of the chemicals. Thus, this experiment also complies with the Antoine Equation.

4.3 Neutralization Titration of Mixture Solution of Propanol and Acetic Acid Reaction Experiment

The objective of this experiment is to choose an optimum temperature to run the adsorptive distillation method experiment. From the literature review, the optimum temperature range to run the experiment is from 40-60°C. For this experiment, six samples are taken every hour for 5 hours for temperatures at 40°C, 50°C and 60°C. The results are shown in the following tables.

T = 40°C						
Time	Initial	Final	Volume (ml)	Volume (l)	M _{mix}	Conversion (%)
0	0	6.8	6.8	0.0068	1.36	4.70
1	6.8	13.9	7.1	0.0071	1.42	0.49
2	13.9	21.1	7.2	0.0072	1.44	-0.91
3	21.1	28.1	7.0	0.0070	1.4	1.89
4	28.1	35.3	7.2	0.0072	1.44	-0.91
5	35.3	42.3	7.0	0.0070	1.4	1.89
T = 50°C						
Time	Initial	Final	Volume (ml)	Volume (l)	M _{mix}	Conversion (%)
0	0.4	7.4	7.0	0.0070	1.4	1.89
1	7.4	14.2	6.8	0.0068	1.36	4.70
2	14.2	21.5	7.3	0.0073	1.46	-2.31
3	21.5	28.5	7.0	0.0070	1.4	1.89
4	28.5	35.4	6.9	0.0069	1.38	3.29
5	35.4	42.3	6.9	0.0069	1.38	3.29
T = 60°C						
Time	Initial	Final	Volume (ml)	Volume (l)	M _{mix}	Conversion (%)
0	0.1	6.5	6.4	0.0064	1.28	10.30
1	6.5	12.8	6.3	0.0063	1.26	11.70
2	12.8	19.1	6.3	0.0063	1.26	11.70
3	19.1	25.5	6.4	0.0064	1.28	10.30
4	25.5	32.0	6.5	0.0065	1.3	8.90
5	32.0	38.3	6.3	0.0063	1.26	11.70

Table 1.10: Conversion of Reaction Mixture

Comparing the results obtained, it can be concluded that the conversion of the reaction increases with temperature. At temperature of 30°C, the highest conversion is around 4.70%. The same goes to conversion at temperature of 40°C. However the range of conversion for 40°C is higher than for 30°C. The highest conversion obtained for temperature at 60°C is 11.70%. So, we will run the adsorptive distillation method using the rotary evaporator at an optimum temperature of 60°C.

4.4 Analysis of Results for Adsorptive Distillation Approach using Rotary Evaporator Experiment

4.4.1 Water Content Analysis

The equipment used for the water content analysis is the Mettler Toledo DL39 Karl Fischer Coulometer. The samples from the adsorptive distillation approach using rotary evaporator experiment are analysed for their water content. The water content percentage of each sample is shown in the following table.

Sample	Weight	Water Content (ppm)	Percentage (%)
1	0.0182	203082.30	20.31
	0.0295	121581.70	12.16
	0.1126	107789.00	10.78
2	0.0192	135879.30	13.59
	0.0323	139050.00	13.91
	0.0719	136572.00	13.66
3	0.0387	111281.00	11.13
	0.1638	111823.60	11.18
	0.0215	107735.60	10.77
4	0.0176	113021.70	11.30
	0.086	122371.10	12.24
	0.162	73389.76	7.34
5	0.0208	80893.80	8.09
	0.0222	51624.76	5.16
	0.0313	114305.00	11.43
6	0.0234	108336.80	10.83
	0.031	86474.52	8.65
	0.0425	43830.84	4.38

Table 1.11: Water Content Percentage in Product

From the results obtained, it can be concluded that the water content of the product is reduced with time. This proves that the molecular sieves adsorb the water from the product. From the graph, the percentage of water content slowly reduces for each of the sample taken.

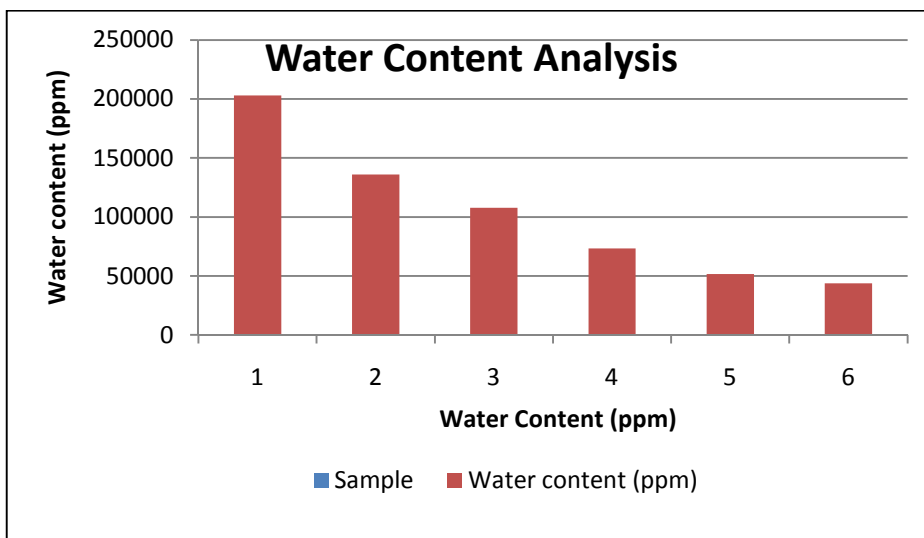


Figure 1.9: Water Content Analysis

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

From the current results, we can conclude that the molecular sieves function to reduce the water content is successful. The main focus of adsorptive distillation is the molecular sieves where it is used to adsorb the water molecules in the reaction to drive the equilibrium of the reaction to the product side, thus producing more products.

The water content of the bio oil is said to be high and is hard to be removed. High water contents will destroy the micro emulsion structure as bio oil has limited solubility in water. By using this method, water is removed and improving the composition and structure of the product that will be obtained.

However, further analysis of the samples will be done to study the composition of the product obtained from the adsorptive distillation approach using the rotary evaporator. Further analysis includes pH, viscosity, density and gas chromatography analysis of the samples.

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APPENDICES

Appendix I

Molecular radius, nm	
Water	0.193
Acetone	0.308

Table 2.1: Molecular radius for water and acetone

(Table data from Alexey B. Nadykto and Fangqun Yu, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 108, NO. D23, 4717)

(<http://www.albany.edu/~yfq/papers/NadyktoYuJGR03.pdf>)

Appendix II

Physical property	Bio-oil	Upgraded bio-oil ^a	Upgraded bio-oil ^a	Diesel Bio-diesel	
Catalyst	—	Nafion [®] SAC13	H ₂ SO ₄	—	—
Kin. viscosity 40 °C, mm ² s ⁻¹	17.0	7.0	7.6	1.2–4.1	1.9–6.0
Water content, wt%	31.5	8.7	4.9	161 ppm	< 0.05 vol%
Flash point, K	326	318	318	333–353	373–443
Density, kg L ⁻¹	1.17	0.95	0.96	0.85	0.88
pH	3.0	3.2	0.5	7.0	7.0
HHV (dry basis), MJ kg ⁻¹	20.6	28.7	27.7	n.a.	n.a

Table 2.2: Product properties of crude bio-oil, upgraded bio-oil, diesel and biodiesel

Appendix III

$$M = \frac{\text{mol}}{\text{volume}(L)}$$

We want to prepare 1.0M of NaOH solution;

Molar mass NaOH : 40g/mol

$$1.0M = \frac{\text{mass}/40}{0.25L}$$

$$\begin{aligned} \text{Mass} &= 0.25 \times 40 \\ &= 10\text{g} \end{aligned}$$

Appendix IV

Mixture solution of 90% mol Butanol and 10%mol Acetic Acid.

Butanol (90 mol)

Molar mass : 74.122 g/mol

Density : 0.8098 g/cm³

$$\begin{aligned}\text{Mass} &= 90 \text{ mol} \times 74.122 \text{ g/mol} \\ &= 6670.98 \text{ g}\end{aligned}$$

$$\begin{aligned}V &= 6670.98 \text{ g} / 0.8098 \text{ g/cm}^3 \\ &= 8237.81 \text{ cm}^3 \\ &= 8237.81 \text{ ml}\end{aligned}$$

Acetic Acid (10mol)

Molar mass : 60.05g/mol

Density : 1.049 g/cm³

$$\begin{aligned}\text{Mass} &= 10 \text{ mol} \times 60.05 \text{ g/mol} \\ &= 600.5 \text{ g}\end{aligned}$$

$$\begin{aligned}V &= 600.5 \text{ g} / 1.049 \text{ g/cm}^3 \\ &= 572.45 \text{ cm}^3 \\ &= 572.45 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{Total Volume} &= 572.45 \text{ ml} + 8237.81 \text{ ml} \\ &= 8810.26 \text{ ml}\end{aligned}$$

We want 150 ml:

$$\begin{aligned}150 \text{ ml} / 8810.26 \\ = 0.01703\end{aligned}$$

Therefore:

$$\begin{aligned}\text{Butanol used} &= 8237.81 \text{ ml} \times 0.01703 \\ &= 140.254 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{Acetic Acid used} &= 572.45 \text{ ml} \times 0.01703 \\ &= 9.746 \text{ ml}\end{aligned}$$

Appendix V

Calculation

Knowing the density of each chemical, assume each chemical is 1ml and weight of chemical can be determined. Thus, total weight of chemicals is calculated and the value is 7.6970g. Here, the mass fraction is determined by using:

$$\text{MassFraction} = (\text{wt}\%) \times (\text{TotalMass})$$

$$\begin{aligned}\text{MassFraction}_{\text{aceticacid}} &= (26.54\%) \times (7.6970) \\ &= 2.0428\end{aligned}$$

Once the mass fraction has been obtained, the volume and total volume will now be calculated. The value of total volume is 8.1154ml. Then, volume ration must be calculated.

$$\text{Volume} = \frac{\text{MassFraction}}{\text{Density}}$$

$$\text{Volume}_{\text{aceticacid}} = \frac{2.0428}{1.0490} = 1.9474$$

$$\text{VolumeRatio} = \frac{\text{Volume}}{\text{TotalVolume}}$$

$$\text{VolumeRatio}_{\text{aceticacid}} = \frac{1.9474}{8.1154} = 0.24$$

After obtaining the volume ratio, it has to be multiplied by 100 in order to get 100ml of artificial bio-oil.