Conversion of Bio-oil to Biodiesel through Reactive Distillation Approach

by

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the requirements for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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In partial fulfillment of the requirement for the
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Approved by,

____

(Assoc. Prof. Dr. Suzana Yusup)

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TRONOH, PERAK
JULY 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 person.

(MOHAMED AFIQ BIN RAMLI)

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ABSTRACT

Anticipated future energy shortage and environmental concerns have boosted researches on alternatives for renewable resource such as biodiesel. Biodiesel or known as fatty acid methyl ester (FAMEs) is produced from esterification process. This project will focus on esterification process between bio-oil and high boiling alcohol which is n-butanol. This project starts with synthesis of bio-oil based on empty fruit bunches (EFB) bio-oil composition. Then, the esterification process between artificial bio-oil and n-butanol is run and tested for physical properties such as density, viscosity, pH and water content. The product of esterification process is analyzed by gas chromatography to check the actual composition as well as to verify the production of biodiesel. The result shows the existence of butyl ester which is biodiesel in end product. However, the physical properties of the product must be improved in term of acidity, and water content.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Nowadays, people are always talking about the shortage of energy source such as petroleum and also the green earth issue. Generally, the rumours of petroleum shortage in Malaysia are spread that it will occur in the period of next fifteen years. Likewise, the usage of petroleum in transportation and industries areas is affecting the environmental issues. The petroleum products are made of the hydrocarbon molecules and highly toxic to many organism, including human. Petroleum also contains trace amounts of sulfur and nitrogen compounds, which are dangerous by themselves and can react with the environment to produce secondary poisonous chemicals. Through the combustion process of petroleum products, carbon monoxide (CO), nitrogen oxides (NO and/or NO_2 , usually referred to as NO_x), sulfur dioxide (SO_2), ground-level ozone (O_3), particulate matter (including things like soot, dust, asbestos fibers, pesticides, and metals), and lead (Pb) will be released to the environment

Anticipated future energy shortages and environmental concerns have boosted research on alternatives for fossil energy carriers. This has encouraged the exploration of renewable resources like bio-mass for energy generation. Flash pyrolysis oil, also known as bio oil, is a biomass-derived liquid energy carrier. It is produced via flash pyrolysis technology in yields up to 75 wt%. A large variety of applications for bio-oil has been proposed. However, poor volatility, high viscosity, coking and corrosiveness of crude bio-oil have limited its applicability (Mahfud et al., 2007). Due to this problem, some improvement in dealing with conversion of bio oil to biodiesel must be applied and one of them is through reactive distillation approach using high boiling alcohol.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Current fuel energy is reducing from time to time and it will be the climate of future energy shortage. The concern of energy shortage and environment has boosted research on alternatives for fossil energy carriers. This encouraged the exploration of renewable resources and one of them is biomass or bio oil. Biomass is one of potential source of fuel for future. Malaysia, offers a huge potential of biomass sources derive from agricultural waste (Hoi and Koh, 2008.). Bio-oil, which is renewable liquid fuel, was harnessed from biomass through pyrolysis. But with original method, the yield is still low with presence of high water and other non-volatile compound. Besides, the current biodiesel is too expensive compared to the conventional diesel in market. This scenario happened due to the low yield of biodiesel conversion using old method of esterification process.

However, the project will focus on applying the reactive distillation approach with presence of high boiling alcohol, n-butanol, and acid catalyst. In fact, the reactive distillation is the latest technology and it combined the reaction process and distillation process at the simultaneously. The conversion’s yield should be improved because of the reaction will favour to the product (right) side. The final product’s properties such as viscosity, heating value, water content, pH and density will be further studied.

1.2.2 Significant of Project

Theoretically, biodiesel can be classified as upgraded bio-oil. After going through the esterification process where the bio-oil is mixed with alcohol by presence of acid catalyst, the biodiesel is formed. Before this process took place, the condition of bio oil is instable particularly for storage purposes. Upgrading process also will try to get rid of the component which deteriorates the stability of bio oil during storage.

As mentioned earlier, the reactive distillation will be used during the entire project. Reactive distillation is designed purposely to get better yield of conversion in term of reactant material and outcome product. The main objective of reactive distillation is to dramatically reduce the use of excess alcohol in the feeding steam, which reduces the cost in downstream alcohol recover processes, and meanwhile maintain a high alcohol-to-oil molar ratio inside of the reactive distillation reactor, which ensures the completion of the esterification of bio-oil to bio-diesel(Singh et al., 2004).

This project is significant because people are trying to research more about renewable sources to generate power in the coming future especially bio oil, so they can further upgrade it and improve its characteristics. In addition to it, renewable biomass sources can be converted to fuels and are a logical choice to replace oil. Likewise, by using biomass as raw material, we can utilize all the waste from agricultural industries into the valuable output. Also, this biodiesel is environmental friendly.

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives

The objectives of this study are:

1. To prove the existence of butyl-ester (biodiesel) as a main product during the esterification between butanol and bio-oil.
2. To characterize the properties of butyl-ester.
3. To test the quality of butyl-ester against conventional biodiesel, fatty acid methyl esters (FAME)

1.3.2 Scope of Study

As outlined in the objectives, the purpose of this project is to convert the bio oil to biodiesel through reactive distillation approach. This project is dealing with esterification process of bio oil and alcohol with presence of acid catalyst. During this process, temperature will play the important role and it will affect the reaction rate. The range of temperature recommended is 323K to 353K. After reaction, the product must be analysed not later than one day to avoid possible changes in the product composition. This final product will be tested on several ways to find out the viscosity, heating value, water content, pH and density All samples have to be stored at 255 K in a refrigerator to prevent further reactions upon storage.

CHAPTER 2

LITERATURE REVIEW

2.1 ANALYSIS OF LITERATURE

The exploration of alternative renewable energy source has been done for many years in order to anticipate the future energy shortage and also as environmental concerns. According to the research and development result, biodiesel is found to be the best alternative to replace the usage of petroleum product for industry and transportation fileds. Biodiesel is best substitute for petro-diesel and also most advantageous over petro-diesel for its environmental friendliness. The quality of biodiesel fuel was found to be significant for its successful use on compression ignition engines and subsequent replacement of non-renewable fossil fuels (Atadashi et al., 2010).

2.1.1 Biodiesel

The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel. The main advantages of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide (Gerpen,2005). Biodiesel reduces net carbon-dioxide emissions by 78% on a life- cycle basis when compared to conventional diesel fuel (Gunvachai et al., 2007). Puppan (2002) has discussed the advantages of biofuels over fossil fuels to be:
(a) availability of renewable sources;
(b) representing CO2 cycle in combustion;
(c) environmentally friendly;
(d) biodegrad-able and sustainable.

Other advantages of biodiesel are as follows: portability, ready availability, lower sulfur and aromatic content, and high combustion characteristics. (Atadashi et al., 2010)

Table 2. 1: Physical property of biodiesel

Physical property	Diesel	Bio-diesel
Kinematic viscosity 40^{o}C, mm^{2}s^{-1}	1.2 — 4.1	1.9 — 6.0
Water content, wt%	161 ppm	<0.05 vol%
Flash point, K	333 --- 353	373 --- 443
Density, kg/L	0.85	0.88
pH	7.0	7.0
HHV (dry basis), MJ/kg	----	----

So far, the use of biodiesel in daily activities is still at the minimum level compared to the petroleum product. This scenario happened because of the economic factor as its price is slightly higher than petroleum products. The insufficient of information about the bio diesel production leads to low yield conversion. The production of biodiesel must meet the standard specifications could either be the American standards for testing materials (ASTM 6751-3) or the European Union (EN 14214). However, the recent researches come out and it shows that this conversion can be improved by applying high boiling alcohol with presence of sulphuric acid during the esterification process.

2.1.2 Bio-oil

Bio-oil is produced through pyrolysis from biomass such as agricultural waste and wood. Biomass is renewable energy that can produce heat and generate electricity. Bio-oil is an attractive alternative energy source. Using biomass feedstock such as wood, the pyrolysis process results in “net zero” carbon dioxide emissions and no sulfoxide emissions. Like petroleum oil, bio-oil can be refined and molded into a wide variety of fuels and chemicals.

Bio-oil based on empty fruit bunches (EFB) is dark brown, free flowing liquids, with an acrid or smoky odour. They are complex mixtures of compounds derived from the depolymerisation of cellulose, hemicelluloses and lignin. Chemically, they have high water content, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds (Mohan et al.,2006).The main acid content inside bio-oil is carboxylic acid. This carboxylic acid will react with alcohol to produce alkyl acetate.

According to Aizuddin(2010), composition of bio-oil is separated to 2 different layer which are lower and upper layer. Most compounds at upper layer are coming from ketone (36%), carboxylic acid (20%), phenol (20%) and followed with aldehyde (8%) and furan (8%). Meanwhile, the lower layer mostly has carboxylic acid (34.15%), phenol (14.63%) and ester (14.63%)

2.2 REACTION

In general, biodiesel is as mono-alkyl esters derived from vegetable oils and animal fats, and alcohols of lower molecular weights in the presence of catalysts. Also, biodiesel can be made through esterification process by mixing the bio-oil and alcohol together with presence of catalyst. The most common general reaction as below:

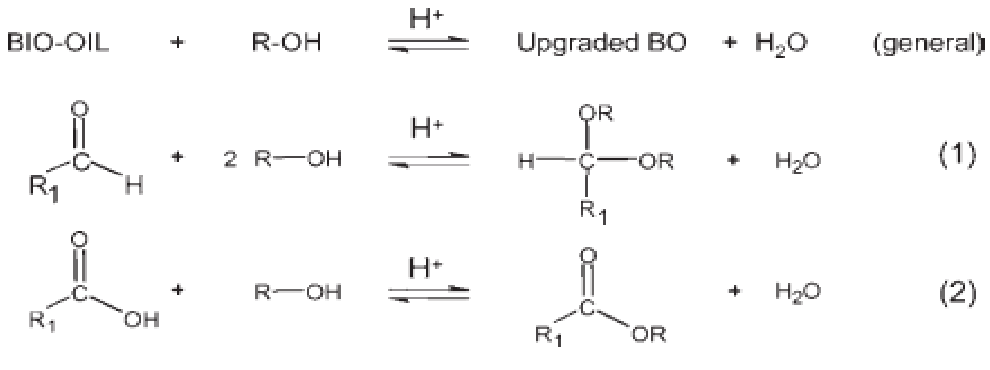


Figure 2. 1: Esterification process

Bio-oil exists in many forms such as carboxylic acid and aldehydes. . 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.

We here propose an alternative upgrading technology for bio oil based on reactive distillation using a high boiling alcohol in the presence of an acid catalyst (Mahfud et al., 2007). The objective is to produce upgraded bio-oil with improved properties like a higher heating value, a lower water content, lower viscosity and lower free acid content. In this new concept, the water in the crude oil as well as the water produced by the various chemical reactions are removed simultaneously (by distillation) in a single step. This will drive the equilibria to completion and is expected to lead to reduced acidity. To prevent excessive alcohol evaporation, alcohols with a boiling point higher than water are required. n-butanol was selected as the alcohol of choice as it is available from renewable resources by fermentation processes.

2.3 REACTIVE DISTILLATION

Reactive distillation (RD) combines chemical reaction and distillation into a single process unit. In some applications particularly in cases when thermodynamic reaction equilibrium prevents high conversions, the coupling of distillation to remove the reaction products from the reaction zone can improve the overall conversion and selectivity significantly. In other applications reactions are utilised to overcome the separation problems caused by azeotropes This combination of reaction and distillation often results into simpler and intensified processes, with less recycle streams and reduced need for waste handling resulting into lower investment and operating costs (Juhaini et al., 1999).

CHAPTER 3

PROJECT METHODOLOGY

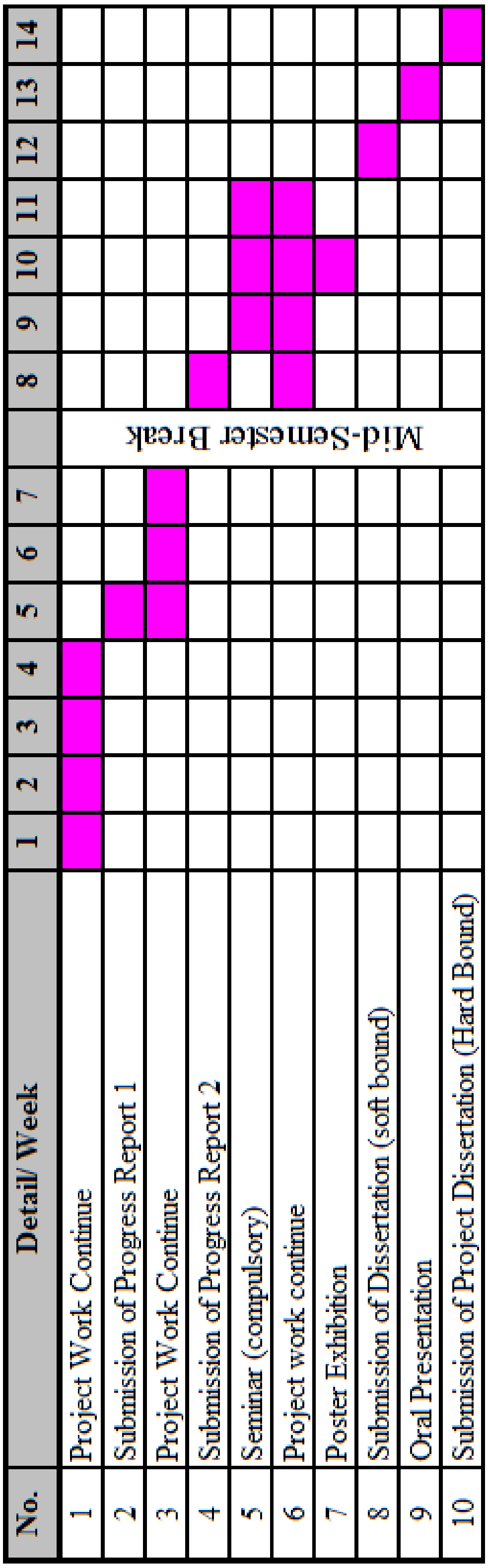
3.1 RESEARCH METHODOLOGY

Table 3. 1: Research methodology

Research Methodology	
Problem Statement	Problem identification on the issue Significance of the project
Literature Review	Review of related research and literature from books and journals Understanding of the concepts of esterification process
Design of Experiment	Decision on material and equipments List the procedure involved
Data Analysis & Interpretation	Evaluation on the result Study on biodiesel properties
Report Writing	Report the finding of the project Conclusion and recommendation

3.2 GANNT CHART

Figure 3.1 below shows the Gantt Chart of this project



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

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Figure 3. 1: Gantt Chart and Milestones for the Project

3.3 EQUIPMENT/APPARATUS

Rotary evaporator, gas chromatography, refrigerator, beakers, scale, Mettler Toledo DL39 Karl Fischer, mikro dropper, Brookfield viscometer and personal protective equipments (PPE).

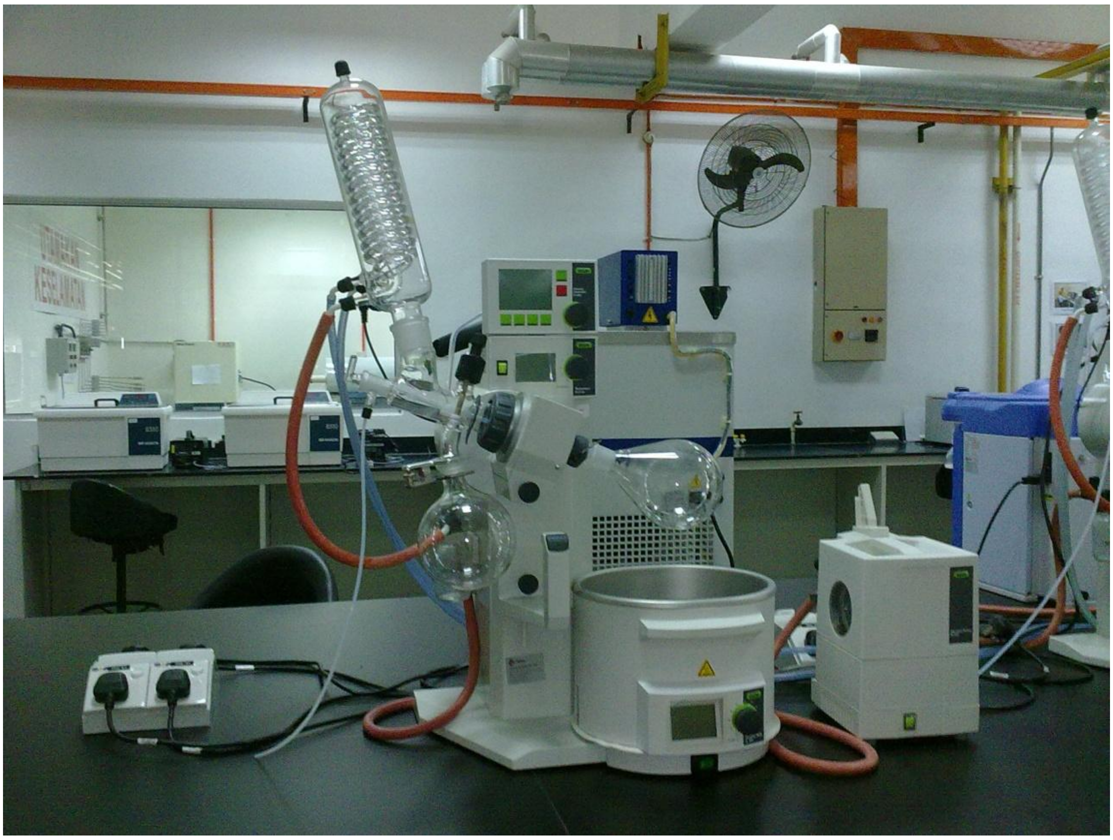


Figure 3. 2: Rotary evaporator

Noted*:

Rotary evaporator system is consisted of water bath as temperature controller,
vacuum pump and distillation column

3.4 CHEMICALS

n-butanol (Merck), Bio-oil, Sulphuric acid 95% - 97% (Merck), n-Butyl acetate GR 99.5% (Merck), Methanol (Merck), 2-Furaldehyde/Furfural ACS Reagent 99% (Sigma Aldirch), Acetic Acid 100% (Merck), Ethyl methyl Ketone (Fisher), Phenol (R&M), Methyl Acetate (R&M), Tetrahydro-Furan (Merck) and 2-Furaldehyde (Sigma Aldirch).

3.5 METHODOLOGY

There are several steps need to be completed to accomplish this project. Thus to study the conversion of bio-oil to biodiesel through reactive distillation approach, the first step is to determine the optimal temperature setting. As for that, the following procedures have been identified and will be used.

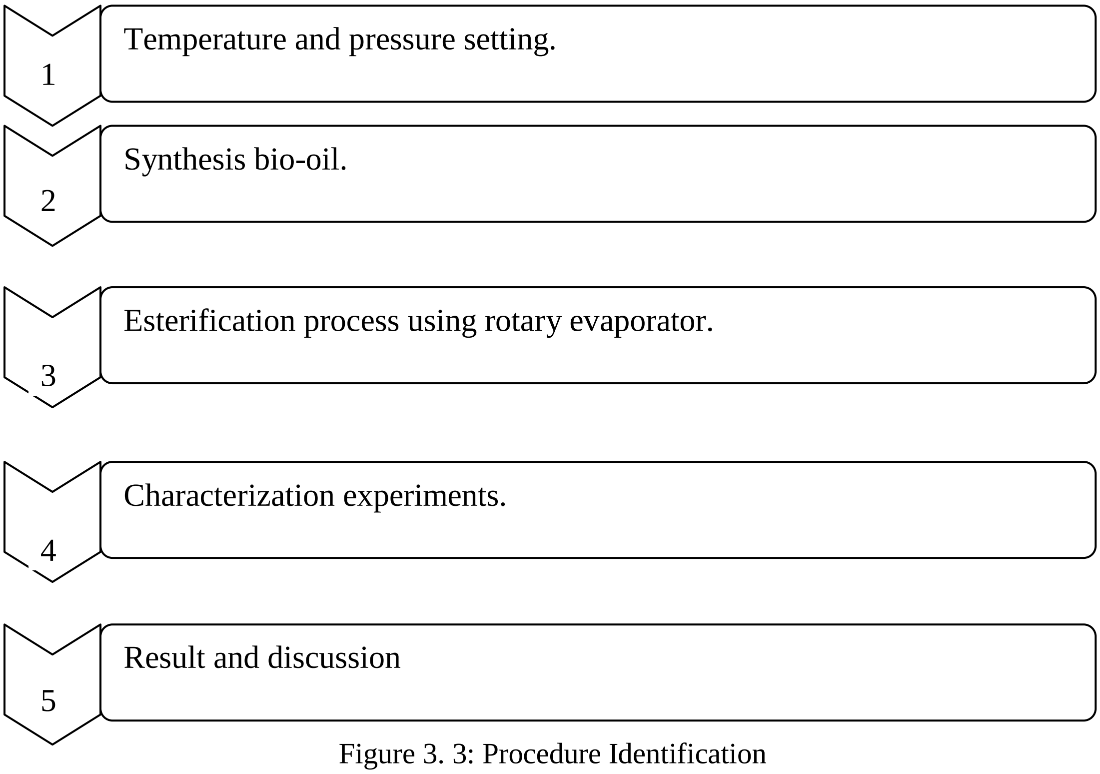


Figure 3. 3: Procedure Identification

3.5.1. Temperature and Pressure Setting

The recommended temperature is the range of 50-70 ^{o}C (323 – 343 K). In order to set the temperature and pressure setting, the properties of the mixture solution must be determined. A neutralization experiment is run over temperature of 30^{o}C, 40^{o}C, 50^{o}C and 60^{o}C in order to determine the optimal temperature of esterification reaction.

Theoretically, product of this esterification is assumed to be butyl acetate which is ester and also a kind of biodiesel. The experiment was done over 5 hours to determine the reaction is completely reaching the equilibrium. 90 mol% of n-butanol was mixed with 10 mol% of acetic acid at desired temperature without any catalyst. For every one hour, a sample of mixture solution was taken out to be neutralized with sodium hydroxide solution. By knowing the volume of titration then, the conversion rate was calculated.

Table 3. 2: Conversion percentage of biodiesel

Experiment	Temperature / ^{o}C	Conversion / %
1	30	15.24
2	40	12.26
3	50	21.19
4	60	27.13

Based on table 3.2, the highest conversion is 27.13% at temperature of 60^{o}C. Thus, 60^{o}C is selected to be the set temperature for esterification process using rotary evaporator.

Using Antoine Equation, temperature and pressure of the reactants can be calculated and determined.

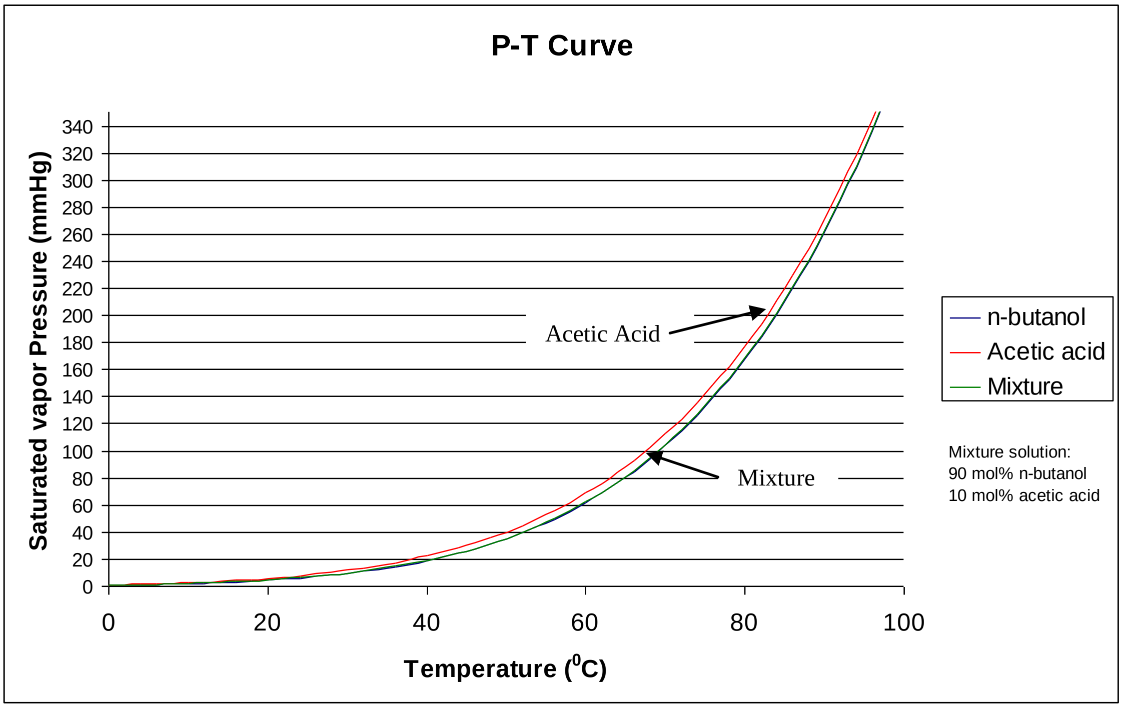


Figure 3. 4: P-T Curve for Reactant

Based on the graph, the exact value of temperature and pressure of the reactant is clearly shown. Graph shows the saturated vapour pressure and temperature (boiling point) of reactants and mixture. Therefore, it will be useful for us in determining the temperature and pressure setting in case of operating and safety purposes. At 60^oC, the boiling point of mixture is 55.6mmHg or 82mbar.

3.5.2 Synthesis Bio-Oil

In order to avoid any damage on the equipment part and due to the unavailability of actual bio-oil, test on actual bio-oil should be postponed. Therefore, the idea of having artificial bio-oil seems to be the best solution for this time. Artificial bio-oil is less in term of viscosity compared to the original one but it has slightly similar compounds' composition of chemical inside.

An alternative mixture based on empty fruit bunches (EFBs) is searched to replace the first method of bio-oil synthesis. Based on GCMS results on bio-oil, a new mixture of artificial bio-oil is found and it consists of acetic acid (26.54%), ethyl methyl ketone (23.63%), phenol (16.98%), tetrahydro furan (6.31%), methanol (5.55%) and 2-furaldehyde (5.12 %) (Y.Aizuddin,2010).

3.5.3 Esterification with Synthesis Bio-oil

Process that bio-oil and alcohol are mixed with presence of acid catalyst. Synthesis bio-oil and n-butanol will be charged into the reactor vessel. The reaction mixture is heated to the desired temperature (60^oC). Using rotary evaporator, 90 mol% of n-butanol (150ml) and 10 mol% of artificial bio-oil (100ml) are mixed into feed column flask. Subsequently, sulphuric acid (1 ml) is added as the catalyst.

The reaction mixture is maintained at the desired temperature using a water bath. The desired pressure typically 80± 2 mbar is set. The starting of the reaction is set at the time for formation of the first drop of distillate in the condensor. A typical reaction time is 60–120 min. Samples are collected for every 30 minutes and named A, B, C and D accordingly.

Table 3. 3 : Product samples labelling

Sample	Time taken, minute
A	30
B	60
C	90
D	150

Supposed sample D is taken at 120 min, but the amount of sample product is low and insufficient. Therefore, the reaction is pro-longed to 150 min. These four samples then undergo the characterization experiments for further analysis.

3.5.4 Characterization Experiments

The purpose of these experiments is to obtain the data for the properties of sample products. Below is the list of experiments that will be conducted for sample product characterization.

1. Density
2. Water content
3. Viscosity
4. pH
5. Gas Chromatography

3.5.4.1 Density

Density of samples is identified using the alternative method by measuring their weight and volume. 0.1 ml of each samples are taken out by mikro dropper and then obtain their weight. The experiment is repeated for 3 times to get the average data. By definition, density is mass over volume; therefore the density can be determined.

Table 3. 4 : Template of result for density test

Sample	Volume (ml)	Weight (g)
A		
B		
C		
D		

3.5.4.2 Water Content

Water content in bio-oil is determined using Karl Fischer titration method. There are 2 types of Karl Fischer titration methods which are volumetric and coulometric titration method. Karl Fischer method utilizes quantitative reaction of water with iodine in presence of lower alcohol. Here, Mettler Toledo DL39, Karl Fischer Coulometer is used. The water content is determined by measuring the amount of iodine consumed as a result of reaction with water in a sample.

Sample is taken out by syringe and measure the initial weight. Then, few drops of sample are injected into Mettler Toledo DL39. Measure back the final weight and find the weight of 3 drops. Mettler Toledo will titrate and ask the weight of 3 drops of sample. Put the weight value and the percentage of water content will appear.

3.5.4.3 Viscosity

Brookfield viscometer is being used to measure the kinematic viscosity. Kinematic viscosity can be converted to dynamic viscosity using density of bio-oil. Using syringe, take a few drops of sample and put them on the test plate. The viscometer will then calculate the kinematic viscosity automatically.

3.5.4.4 pH

The pH of samples product is measured directly by using pH meter. The electrode is immersed into the samples. Data will be recorded into table and discussed.

Table 3. 5 : Template of result for pH test

Sample	pH
A	
B	
C	
D	

3.5.4.5 Gas Chromatography Analysis

Once the product obtained, it will further analyze by gas chromatography (GC) to validate and determine the biodiesel. The product might form in many liquid phase layers with different compounds. Therefore, it is necessary to validate and determine biodiesel compound as well as the yield of conversion. Graph of GC will be further analyzed.

3.5.5 Esterification with Actual Bio-oil

Similar to previous esterification process, at this time, the reactant used is actual bio-oil and n-butanol. 172ml of bio-oil (10mol %) and 128ml of n-butanol (90mol %) are mixed in rotary evaporator with presence of 1ml of sulphuric acid as catalyst. Before that, bio-oil is diluted first with tetra hydro furan (THF) by volume ratio of 2:8 for safety purposes. The temperature and pressure are set to be 60^{o}C and 80mbar. The process is being carried on for 90 minutes with reflux ration of 75%. End product will be analyzed using GCMS.

CHAPTER 4

RESULT AND DISCUSSION

4.1 SYNTHESIS BIO-OIL

Samples product is taken at product column, which is at the bottom of condenser. 75% of total reflux is applied on this esterification process. At the end, a colourless solution with 2 different liquid layers is obtained as the product. The upper layer is ester rich and the lower layer is water rich.

Figure 4. 1: Sample of product

4.1.1 Gas Chromatography

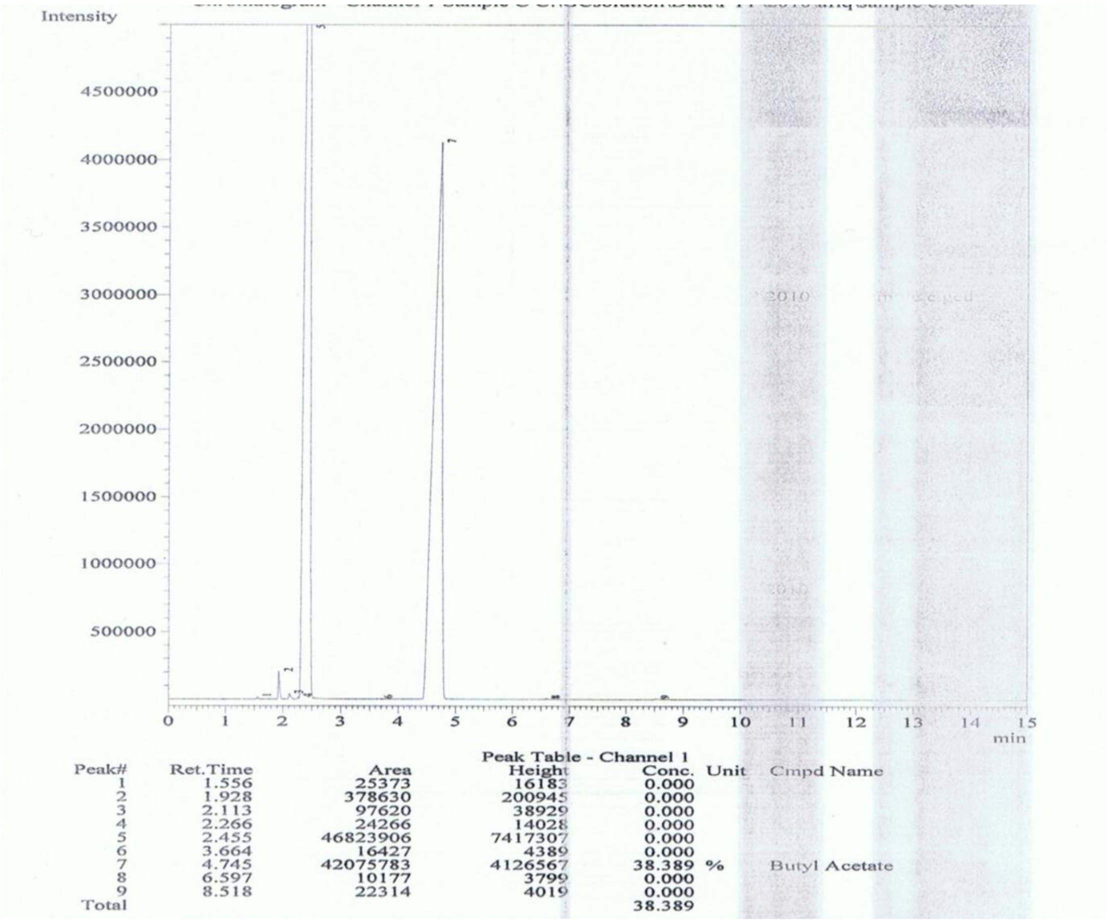
The purpose of gas chromatography is to validate the existence of butyl ester which is biodiesel in sample of product A, B, C and D. GC analysis will detect and give actual composition through output graph. Beside samples of product, the expected product or chemicals are also injected to GC equipment. The matching will be automatically done by GC by comparing the area under the peak and the peak itself. Another thing, GC can find the concentration of sample product. By knowing the concentration, the best time duration for experiment running can be determined. Table 4.1 shows the result of GC analysis;

Table 4. 1: GC-FID Analysis on Sample Product

Sample	Time taken, min	Concentration, %
A	30	9.517
B	60	24.708
C	90	38.389
D	150	27.473

Table 4.1 shows the GC result of sample product. From GC graph, each sample has almost 6 peaks. Each peak has different size and area under the peak. The area under the peak indicates the concentration of each chemical in the sample. Knowing the feed and the reaction, expected product that coming out from reaction can be determined. In this artificial bio-oil experiment, the expected product is n-butyl acetate which is ester and also biodiesel.

From table 4.1, the concentration of n-butyl acetate on sample C is the highest. Meanwhile, concentration of n-butyl acetate on sample D is slightly reduced even though the time for sample D is longer than sample C. The only assumption that can be made is the esterification process is reversible process and will convert the product back to the reactant.



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Unit	Cmpd Name
1	1.556	25373	16183	0.000		
2	1.928	378630	200945	0.000		
3	2.113	97620	38929	0.000		
4	2.266	24266	14028	0.000		
5	2.455	46823906	7417307	0.000		
6	3.664	16427	4389	0.000		
7	4.745	42075783	4126567	38.389	%	Butyl Acetate
8	6.597	10177	3799	0.000		
9	8.518	22314	4019	0.000		
Total				38.389		

Figure 4. 2: Peaks of Sample C

4.1.2 Density

Table 4.2 shows the density of each sample. The density is kept changing over the time and it increasing from sample A to sample C. However, density is decreasing to the original on sample D. This pattern indicates the reaction of n-butanol and bio-oil still occurred over time. Density is kept changing because the chemical composition inside the sample product is changed over the time.

Table 4. 2: Density of sample product

Sample	Density, g/ml
A	0.8713
B	0.9670
C	0.9980
D	0.8700

From literature, the density value for fatty acid methyl ester (biodiesel) is within the range of 0.88 g/ml. From GC analysis, the existence of biodiesel in sample product has been proved. However, the density recorded for sample product is not close to conventional biodiesel. Using synthesis bio-oil which having only acetic acid as main portion of carboxylic component, we can not expect to have similar properties with FAME (biodiesel).

4.1.3 Water Content

From general equation earlier, it stated that this esterification reaction will give biodiesel, by product and water. Means, water is produced and it will contribute to the sample product composition.

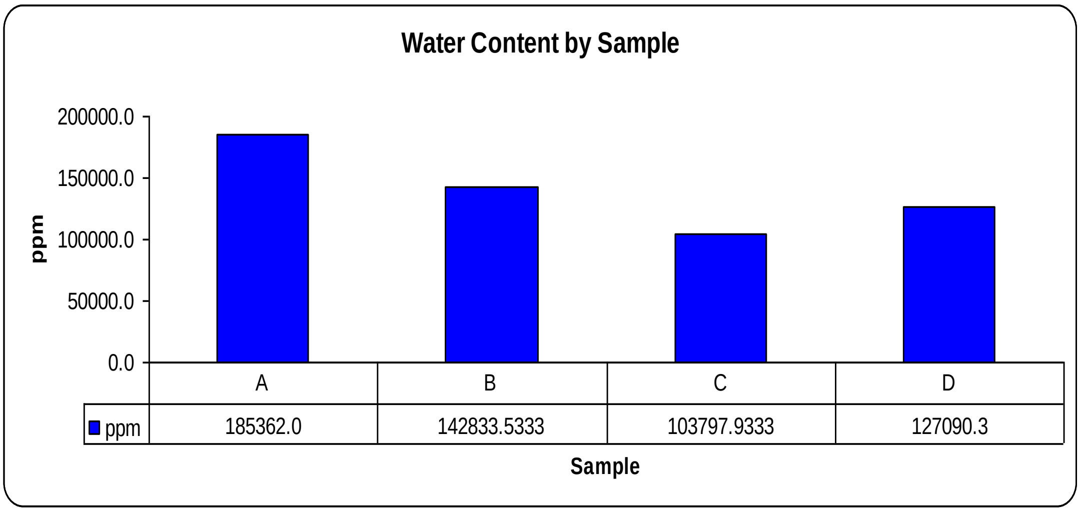


Figure 4. 3: Water Content by Sample Product

Based on the graph, the lowest water content is sample C which is 10397.93 ppm or 10.3%. Figure 6 also shows the amount of water content decreasing from A to C but increasing back at sample D. Actually, the sampling is related to the time of experiment. From here, it shows that 90 min is the best time for the esterification process can be run to get the lowest water content as possible. The percentage of water content % for very small compared to this result. But, some improvement can be taken to cater the problem in term of water content percentage.

4.1.4 Viscosity

In this experiment, the viscosity is tested with Brookfield viscometer. However, the viscometer can not determine the actual samples' viscosity. The samples are too diluted and the viscometer can not calibrate the viscosity below than 20cP. Another alternative to find the viscosity is by using Ubbelohde viscometer. But, it need large amount of sample.

4.1.5 pH

The result of pH test indicates samples product are acidic. The pH value is less than 7 and its around 4.1 to 4.4. The acidity is lesser compared to the bio-oil which is around pH of 3, means the corrosiveness is reducing. Table 4.3 shows the acidity is increasing over the time. Acidity of sample C is the highest which is pH of 4.103. From literature, n-butyl ester is acidic. More n-butyl ester present in sample will result to the lower pH value. pH value for sample D can not be determined due to the small amount of sample and the immersion of electrode can not be done.

Table 4. 3: pH result

Sample	pH
A	4.333
B	4.242
C	4.103
D	-

Compared to the pH value for fatty acid methyl ester, this value of 4.242 is too corrosive. The best pH value is 7.0 which is neutral. Means, neutralization and separation need to be taken to reduce the acidity.

4.2 ACTUAL BIO-OIL

After 90 minutes of esterification process, end product is then being analyzed by gas chromatography mass spectrum (GCMS). The analysis from GCMS as below:

Table 4. 4: GCMS Analysis on actual bio-oil end product

Peak	Component	Percentage, %
1	1-Hydroxy-2-butanone	1.351
2	Cyclopentanone	0.403
3	Acetic acid, butyl ester	75.295
4	2-Cyclopenten-1-one	0.359
5	2-Propanone, 1-(acetyloxy)	0.318
6	n-butyl ether	0.549
7	2-Cyclopenten-1-one, 3-methyl	0.734
8	Propanoic acid, butyl ester	7.764
9	4-Heptanone, 3-methyl	0.494
10	Phenol	0.758
11	Butanoic acid, butyl ester	1.434
12	1,3-Dioxane,4-methyl	8.436
13	Phenol, 2-methoxy	0.386
14	Benzenamine, 2,5-difluoro	0.597
15	2-Butanone, 4,4-dimethoxy	0.838

Based on table 4.4, the reaction between actual bio-oil with n-butanol gives end product of butyl ester more than 87%.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Actual bio-oil is not available during the experiment setup and plus, the danger of high viscous bio-oil, artificial bio-oil is replaced as main reactant for esterification process of upgrading bio-oil. Synthesis bio-oil is prepared as close as possible to the composition of actual bio-oil. It is a fundamental of study to create an alternative way but maintain the properties of actual one. From the results, both GCMS and GC-FID indicate the existence of butyl ester in synthesis and actual bio-oil’s end product. It concludes that the esterification process between n-butanol and bio-oil will produce biodiesel which is butyl ester.

5.2 RECOMMENDATION

Result from product characterization shows that the sample product is still slightly acidic and high water content. Therefore, neutralization and adsorbent must be applied to cater these issues.

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APENDICES

APENDICE A

Table A- 1: Antoine Equation Coefficient

Component	A	B	C
n-butanol	7.2906	1282.8500	173.2470
Acetic Acid	7.27642	1326.65	183.913

$$\boxed{\log P^{*}_{Saturatedvapor} = A - \frac{B}{T + C}}$$

n-butanol;
At T= 40^{o}C

$$P^{*}_{saturatedvapor} = 10\text{^}(7.2906 - \frac{1282.85}{173.247 + 20})$$

$$=18.8290 \text{ mmHg}$$

Table A- 2: Saturated vapor pressure

T / ^{0}C	n-butanol		acetic acid	
	log P	P (mm Hg)	log P	P (mm Hg)
0	-0.1141	0.7689	0.0630	1.1560
20	0.6522	4.4898	0.7705	5.8947
40	1.2748	18.8290	1.3516	22.4685
60	1.7907	61.7528	1.8374	68.7687
80	2.2250	167.8851	2.2496	177.6536
100	2.5958	394.2607	2.6037	401.5002

Mixture solution:
90 mol% n-butanol
10 mol% acetic acid

$$\boxed{P^{*}_{saturatedvapor,mixture} = \sum p^{*}_{saturatedvapor,i} x_i}$$

At T=40^{o}C,

$$P^{*}_{saturatedvapor} = (0.9*18.8290)+(0.1*22.4685)$$

$$=19.1929 \text{mmHg}$$

Table A- 3:Saturated vapor pressure for mixture solution

T / ^{0}C	$p_i x_{butanol}$	$p_i x_{H2SO4}$	P(mmHg)
0	0.6920	0.1156	0.8076
20	4.0408	0.5895	4.6303
40	16.9461	2.2469	19.1929
60	55.5775	6.8769	62.4544
80	151.0966	17.7654	168.8619
100	354.8346	40.1500	394.9846

APENDICE B

CALCULATION

19.9ml of 1.0M NaOH is used to neutralized 1ml of Acetic Acid

$$M_{NaOH} V_{NaOH} = M_{Acetic} V_{Acetic}$$

$(0.0199)(1.0) = (0.001)(M_{Acetic})$

$$M_{Acetic} = \frac{(0.0199)(1.0)}{0.001}$$

M_{Acetic} = 19.9M

Since 10ml of Acetic Acid is diluted in 150 mixture solution, therefore:

$$M_{Mixture} V_{Mixture} = M_{Acetic} V_{Acetic}$$

$(M_{Mixture})(0.148) = (19.9)(0.01)$

$$M_{Mixture} = \frac{(19.9)(0.01)}{0.148}$$

$M_{Mixture}$ = 1.345M

$M_{Mixture}$ = Initial concentration of mixture solution

$$Conversion = \frac{M_{Initial} - M_{Final}}{M_{Initial}}$$

M_{Final} = Concentration of mixture every on hour

Example:

5.8ml of 1.0NaOH is used to neutralize 5ml of mixture solution after 1 hour in experiment 1:

$$M_{NaOH} V_{NaOH} = M_{Mixture} V_{Mixture}$$

$(M_{Mixture})(0.005) = (1.0)(0.0058)$

$$M_{Mixture} = \frac{(1.0)(0.0058)}{0.005}$$

$M_{Mixture}$ = 1.16M

$$Conversion = \frac{1.345 - 1.16}{1.345} X\,100\,\%$$

$Conversion$ = 13.75%

Table A- 4: Experiment at 30^{o}C

Time (hr)	V_{NaOH} (ml)	Conversion(%)
0	11.8	-75.465 (not well-mixed)
1	5.8	13.755
2	5.7	15.242
3	5.9	12.268
4	6.0	10.781
5	5.8	13.755

Table A- 5: Experiment at 40^{o}C

Time (hr)	V_{NaOH} (ml)	Conversion(%)
0	11.6	-72.491 (not well-mixed)
1	5.9	12.268
2	5.9	12.268
3	5.9	12.268
4	5.9	12.268
5	6.0	10.781

Table A- 6: Experiment at 50^{o}C

Time (hr)	V_{NaOH} (ml)	Conversion(%)
0	5.5	18.216
1	5.3	21.190
2	5.6	16.729
3	5.6	16.729
4	5.8	13.755
5	5.4	19.703

Table A- 7: Experiment at 60^{o}C

Time (hr)	V_{NaOH} (ml)	Conversion(%)
0	5.1	24.164
1	5.0	25.651
2	5.0	25.651
3	4.9	27.138
4	5.0	25.651
5	4.9	27.138