

# **Conversion of Bio Oil to Bio Diesel Through Reactive Distillation Approach**

by

Mohamad Azril Bin Mohd Radzali (11597)

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

MAY 2011

Universiti Teknologi PETRONAS  
Bandar Seri Iskandar  
31750 Tronoh  
Perak Darul Ridzuan

## **ABSTRACT**

This report is about an understanding about the final year project topic entitled 'Conversion of Bio-Oil to Biodiesel through Reactive Distillation Approach'. The method consist of treating bio-oil with a high boiling alcohol like n-butanol in the presence of a (solid) acid catalyst at 323k – 353k under reduced pressure (<10kPa).

The future energy shortage has started the exploration of renewable energy source such as biodiesel. Biodiesel is mono-alkyl esters derived from vegetable oils and animal fats, and alcohols of lower molecular weights in the presence of catalysts. Biodiesel can be made through esterification process by mixing the bio oil and alcohol together with presence of catalyst.

The yield of conversion must be improved and also the reactant material has to be optimized. For the first chapter of this progress report, it will cover the information regarding the problem statement and also the background of study. Meanwhile, the theory and literature reviews will be explained on second chapter. The definition of biodiesel, bio oil and the reactive distillation are being further explained on this section. At last, this report is describing the methodology used in this project. The comparative studies will be applied to test the sample of biodiesel product.

## **ACKNOWLEDGEMENTS**

I am heartily thankful to my supervisor, Dr Suzana Yusup, whose encouragement, guidance and support from the initial to the final level enabled me to develop and understanding of this Final Year Project II.

Then I would like to thank to Dr Umer for guiding me throughout this FYP 1. I have some difficulties in doing this project, but he taught me patiently until I knew what to do. He never gives up on giving me advice regarding the FYP1 matters.

I would also like to thank technicians of chemical department and bio hydrogen lab for helping me with the test and equipments in order for me to conduct my project smoothly without any difficulties.

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.

# TABLE OF CONTENT

|  |     |
|--|-----|
| ABSTRACT .....                             | i   |
| LIST OF TABLE .....                        | iii |
| LIST OF FIGURE.....                        | iii |
| CHAPTER 1.....                             | 1   |
| INTRODUCTION .....                         | 1   |
| 1.1 Background of Study.....               | 1   |
| 1.2 Problem Statement.....                 | 2   |
| 1.3 Objectives and Scope of Study.....     | 3   |
| 1.3.1 Objectives.....                      | 3   |
| 1.3.2 Scope of Study .....                 | 3   |
| CHAPTER 2.....                             | 4   |
| LITERATURE REVIEW .....                    | 4   |
| 2.1 Analysis of Literature .....           | 4   |
| 2.1.1 Biodiesel.....                       | 4   |
| 2.1.2 Bio Oil.....                         | 5   |
| 2.2 Reaction.....                          | 6   |
| 2.3 Reactive Distillation .....            | 7   |
| CHAPTER 3.....                             | 8   |
| PROJECT METHODOLOGY.....                   | 8   |
| 3.1 Research Methodology.....              | 8   |
| 3.2 Gantt Chart .....                      | 9   |
| 3.3 Equipment/Apparatus .....              | 10  |
| 3.4 Materials .....                        | 11  |
| 3.4.1 Bio Oil.....                         | 11  |
| 3.4.2 Alcohol.....                         | 11  |
| 3.4.3 Acid catalyst.....                   | 11  |
| 3.5 Methodology.....                       | 13  |
| 3.5.1 Esterification .....                 | 13  |
| 3.5.2 Gas Chromatography Analysis.....     | 14  |
| 3.5.3 Study of Bio diesel properties ..... | 15  |

|                                    |    |
|------------------------------------|----|
| CHAPTER 4.....                     | 16 |
| RESULT AND DISCUSSION .....        | 16 |
| CHAPTER 5.....                     | 21 |
| CONCLUSION AND RECOMMENDATION..... | 21 |
| REFERENCES.....                    | I  |
| APENDICES.....                     | II |

### **LIST OF TABLE**

|  |    |
|--|----|
| Table 1: Physical Property of Bio Diesel .....                   | 5  |
| Table 2: Research Methodology .....                              | 8  |
| Table 3: Gantt Chart and Milestones for the Project.....         | 9  |
| Table 4: Result of GC Analysis.....                              | 17 |
| Table 5: Chemical Composition of Major Bio Oil Constituents..... | 18 |
| Table 6: Result of Density Analysis.....                         | 19 |
| Table 7 : Result of Water Content Analysis.....                  | 19 |
| Table 8 : Result of pH Analysis .....                            | 20 |

### **LIST OF FIGURE**

|  |    |
|--|----|
| Figure 1: Esterification Process.....      | 6  |
| Figure 2: Rotary Evaporator.....           | 11 |
| Figure 3: Bio Oil .....                    | 12 |
| Figure 4: Overview Process Diagram .....   | 13 |
| Figure 5: P-T Curve for Reactant .....     | 14 |
| Figure 6: Sample of Product.....           | 16 |
| Figure 7: GC Analysis Peak Result.....     | IV |
| Figure 8: GC Analysis (Area Percent) ..... | V  |

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

The usage of petroleum in transportation and industries areas is giving bad effect to the environment. 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 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<sub>2</sub>), usually referred to as NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), ground-level ozone (O<sub>3</sub>), particulate matter (including things like soot, dust, asbestos fibers, pesticides, and metals), and lead (Pb) will be released to the environment (Oil Spill Intelligence Report, 1997)

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 BO have been proposed. However, poor volatility, high viscosity, coking and corrosiveness of crude BO have limited its applicability (F.H. Mahfud, 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**

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 W.K, 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 transesterification 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.

## **1.3 Objectives and Scope of Study**

### 1.3.1 Objectives

The objectives of this study are:

1. To prove the existence of biodiesel as a main product during the esterification between butanol and bio-oil with presence of acid catalyst.
2. To characterize the properties of the esterification product.
3. To compare the quality of treated bio oil 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 fields. 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 (A. Abdul Aziz, 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 JV,2005). Biodiesel reduces net carbon-dioxide emissions by 78% on a life- cycle basis when compared to conventional diesel fuel (Hassan, 2007). Puppan (Puppan, 2002) has discussed the advantages of biofuels over fossil fuels to be: (a) availability of renewable sources; (b) representing CO<sub>2</sub> cycle in combustion; (c) environmentally friendly; and (d) biodegrad-able and sustainable. Other advantages of biodiesel are as follows: portability, ready availability, lower sulfur and aromatic content, and high combustion characteristics. (A. Abdul Aziz, 2010)

**Table 1: Physical Property of Bio Diesel**

| Physical property   | Diesel      | Bio-diesel  |
|---|-------------|-------------|
| Kinematic viscosity 40°C, mm <sup>2</sup> s <sup>-1</sup> | 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 bio diesel 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

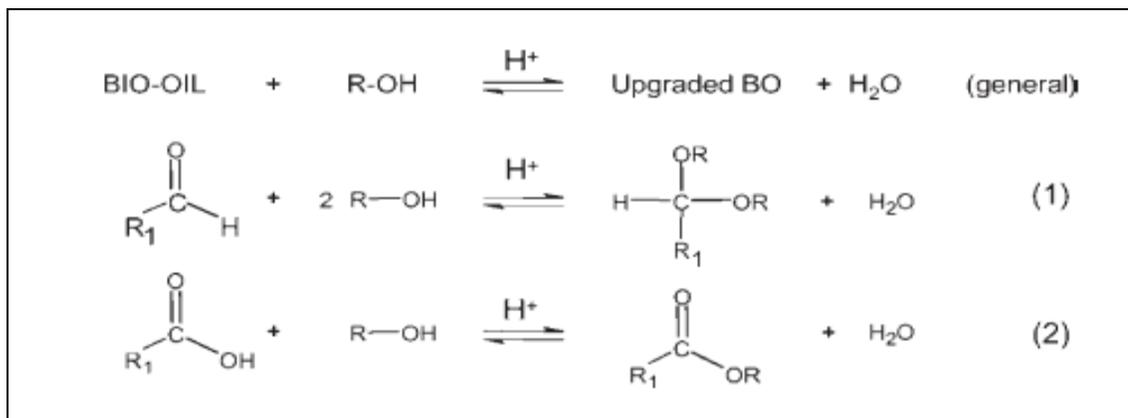
Bio oil is produced through pyrolysis from biomass such as agricultural waste and wood. Biomass is renewable energy that can produce heat and generate electricity. Bio-oil is an attractive alternative energy source. Using biomass feedstock such as wood, the pyrolysis process results in “net zero” carbon 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 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,2006).The main acid content inside Bio oil is acetic acid. This acetic acid will react with alcohol to produce alkyl acetic.

## 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 BO and alcohol together with presence of catalyst. The most common general reaction as below:



**Figure 1: Esterification Process**

Bio oil exists in many forms such as acetic 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 (F.H. Mahfud,

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, 1999).

# CHAPTER 3

## PROJECT METHODOLOGY

### 3.1 Research Methodology

**Table 2: Research Methodology**

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

### 3.2 Gantt Chart

Table 3: Gantt Chart and Milestones for the Project

| No. | Detail/ Week                                    | 1 | 2 | 3 | 4 | 5 | 6 | 7 |   | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |   |
|-----|---|---|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|---|
| 1   | Project Work Continues                          |   |   |   |   |   |   |   | M<br>i<br>d<br>-<br>S<br>e<br>m<br>e<br>s<br>t<br>e<br>r<br><br>B<br>r<br>e<br>a<br>k |   |   |    |    |    |    |    |    |   |
| 2   | Submission of Progress Report                   |   |   |   |   |   |   |   |   | ● |   |    |    |    |    |    |    |   |
| 3   | Project Work Continues                          |   |   |   |   |   |   |   |   |   |   |    |    |    |    |    |    |   |
| 4   | Pre-EDX   |   |   |   |   |   |   |   |   |   |   |    |    | ●  |    |    |    |   |
| 5   | Submission of Draft Report                      |   |   |   |   |   |   |   |   |   |   |    |    |    | ●  |    |    |   |
| 6   | Submission of Dissertation (soft bound)         |   |   |   |   |   |   |   |   |   |   |    |    |    |    | ●  |    |   |
| 7   | Submission of Technical Paper                   |   |   |   |   |   |   |   |   |   |   |    |    |    |    | ●  |    |   |
| 8   | Oral Presentation                               |   |   |   |   |   |   |   |   |   |   |    |    |    |    |    | ●  |   |
| 9   | Submission of Project Dissertation (Hard Bound) |   |   |   |   |   |   |   |   |   |   |    |    |    |    |    |    | ● |

● Suggested Milestone  
 Process

### 3.3 Equipment/Apparatus

Rotary evaporator, gas chromatography, refrigerator, beakers, scale and personal protective equipments (PPE).



**Figure 2 : Rotary Evaporator**

Note :

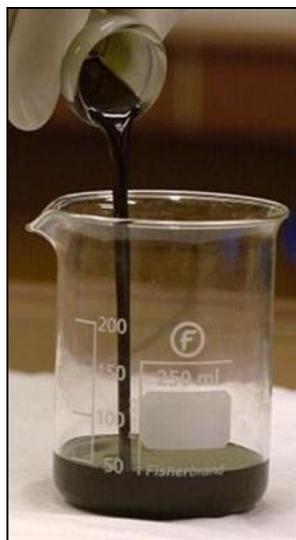
Rotary evaporator system is consisted of water bath as temperature controller, vacuum pump and distillation column

### 3.3 Materials

#### 3.4.1 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 sulphoxide emissions. Like petroleum oil, bio-oil can be refined and molded into a wide variety of

fuels and chemicals. The most portion of bio oil is coming from acetic acid, therefore acetic acid is chosen as bio oil in this project.



**Figure 3: Bio Oil**

### **3.4.2 Alcohol**

n-butanol will be used as reactant during esterification process. From literature review, the method requires an alcohol with a boiling point higher than water. To prevent solidification/polymerization of the bio oil at elevated temperature, the procedure is applied under reduced pressure. Therefore, the hypothesis of using high boiling alcohol can be tested.

### **3.4.3 Acid catalyst**

Sulphuric acid is chosen to be used as catalyst for this project. From a chemical point of view, it is anticipated that reactive molecules like organic acids (sulphuric acid) is converted by the reactions with alcohols to esters.

### 3.5 Methodology

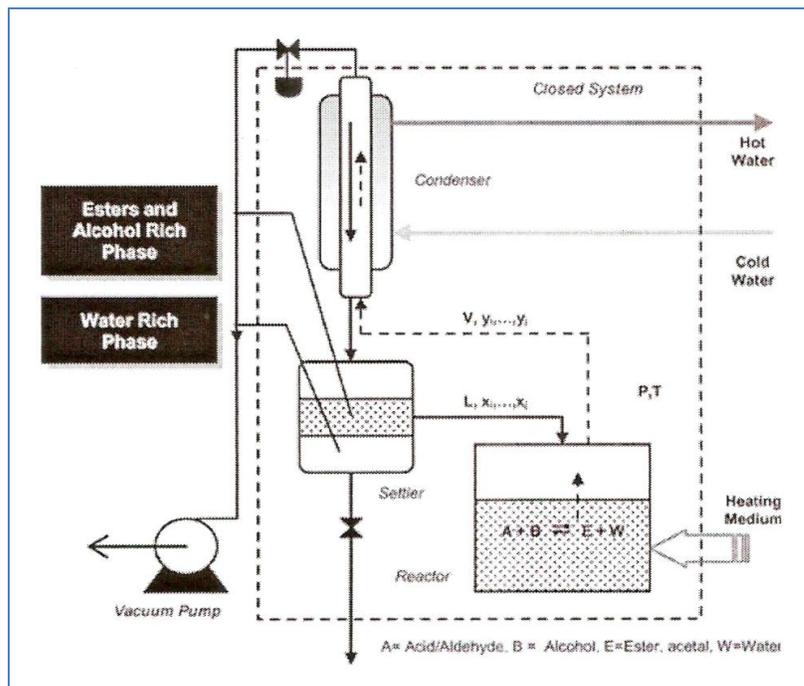


Figure 4: Overview Process Diagram

#### 3.5.1 Esterification

Process that bio oil and alcohol are mixed with presence of acid catalyst. BO (10 ml) and n-butanol (15 ml) will be charged into the reactor vessel. The reaction mixture is heated to the desired temperature (323–353 K). Subsequently, the catalyst (1.6 wt%) will be added. The reaction mixture is maintained at the desired temperature using a water bath. The desired pressure typically 5+0.05 kPa is set. The starting of the reaction is set at the time for formation of the first drop of distillate in the condenser.

A typical reaction time is 30–60 min. After first trial, proceed the same procedures with low boiling alcohol, ethanol. During entire experiment, PPE must be equipped.

##### 3.5.1.1 Temperature and Pressure

The recommended temperature is the range of 50-70 °C (323K – 343K). For this experiment the exact temperature used is 60 °C. In order to set the temperature and pressure setting, the properties of the mixture solution must be determined. Using

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

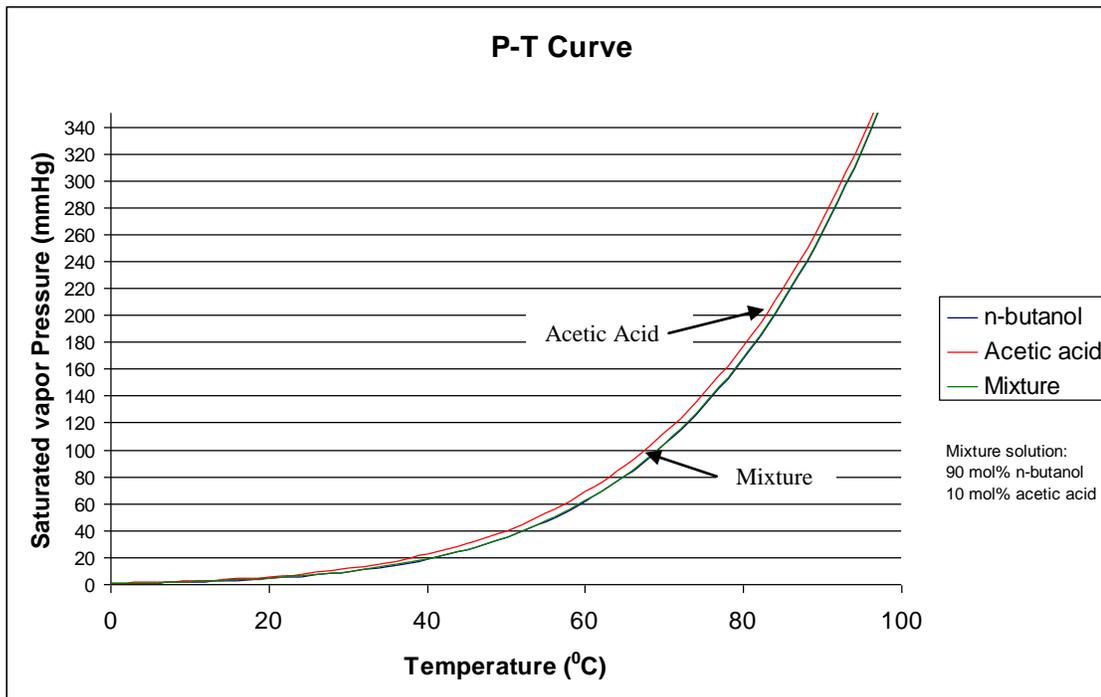


Figure 5: P-T Curve for Reactant

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.

### 3.5.2 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 validate biodiesel compound as well as the yield of conversion. Graph of GC will be further analyzed.

### **3.5.3 Study of Bio diesel properties**

#### *3.5.3.1 Water Content Experiment*

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. The water content is determined by measuring the amount of iodine consumed as a result of reaction with water in a sample.

#### *3.5.3.2 Viscosity Experiment*

Capillary viscometer is being used to measure the kinematic viscosity. Kinematic viscosity can be converted to dynamic viscosity using density of bio oil. Fill the viscometer with bio oil and immerse the viscometer into bath of water. It contains a few tubes and the time for liquid to flow from one mark to the other at the tube to measure its viscosity using stop watch.

#### *3.5.3.3 pH Experiment*

Titration is a general class of experiment where a known property of one solution is used to infer an unknown property of another solution. In acid-base chemistry, we often use titration to determine the pH of a certain solution. This experiment involves apparatus like burette and cone flask. We use this instrumentation to calculate the amount of unknown acid in the receiving flask by measuring the amount of base, or titrant, it takes to neutralize the acid.

#### *3.5.3.4 Density Experiment*

ASTM D 1298 is a standard method to measure the density using glass hydrometer. This test method is also suitable for bio oil, viscous liquid by allowing sufficient time for BO to reach equilibrium. Values are measured on a hydrometer at either the reference temperature or at another convenient temperature, and readings corrected to the reference temperature and values determined as density, relative density, or API gravity can be converted to equivalent values in the other units.

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Synthesis of Bio-Oil

The experiment has been conducted 3 times. 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. Based on theoretical the treated bio oil with alkyl ester (bio diesel) is the upper layer because of the density is less compared to the water rich at bottom layer.



**Figure 6: Sample of Product**

Since the original bio-oil used is very limited, the experiment conducted has been downscale in term of volume percentage. The experiment was conducted 3 times. The first one was 15 minutes reaction time and the second one was 30 minutes reaction time. The third one is supposed to be conducted with 45 minutes however because of the volume had been downscale, the solution was completely saturated just after 30 minutes and reaction time cannot be more than 30 minutes. Because of the downscale of the

volume percentage used, the volume of the final product collected was quite small. After product has been collected, several tests were conducted for the product.

#### 4.1.1 Gas Chromatography

The purpose of gas chromatography is to validate the existence of alkyl ester which is biodiesel in the sample of the product, GC analysis will detect and give actual composition through output graph. After that the matching will be automatically done by comparing the area under the peak with the one in the GC library. After the comparison, the result of the concentration of each composition is known. Table 3 shows the result of GC analysis:

**Table 4: Result of GC Analysis**

| Peak no.  | Composition   | Concentration (%) |
|-----------|---|-------------------|
| 1         | Cyclohexanecarboxylic acid, 4-pentyl-, 2,3-dicyano-4- (pentylloxy) phenyl ester, (E) -    | 1.17              |
| <b>2</b>  | <b>9-Octadeconic acid-, methyl ester,</b>   | <b>13.03</b>      |
| <b>3</b>  | <b>9-Octadeconic acid (z) -, methyl ester,</b>  | <b>24.39</b>      |
| <b>4</b>  | <b>7,10 – Octadecadienoic acid, methyl ester</b>  | <b>10.02</b>      |
| 5         | 2-Benzofurancarboxylic acid, 2,4,5,6,7,7a-hexahydro-4,4,7a-trimethyl-, methyl ester, cis- | 4.65              |
| 6         | 3,4 – Dimethoxy-dl-phenylalanine  | 4.68              |
| <b>7</b>  | <b>9,12-Octadecadienoic acid, methyl ester</b>  | <b>13.85</b>      |
| 8         | 1,3,6 – Trimethyladamantane   | 1.64              |
| <b>9</b>  | <b>Undecanoic acid, methyl ester</b>  | <b>2.79</b>       |
| 10        | Methyl 9,10-epoxyoctadecanoate  | 2.20              |
| <b>11</b> | <b>Octadecanoic acid, 10-oxo, methyl ester</b>  | <b>17.15</b>      |
| 12        | Bicyclo heptanes-3-one, 2,6,6-trimethyl -   | 8.78              |
| 13        | 1,2-Benzenedicarboxylic acid, mono (2-ethyhexyl) ester                                    | 1.78              |
| 14        | 1-Napthalenecarboxamide, N,N-dimethyl -   | 1.16              |

|    |   |      |
|----|---|------|
| 15 | 10- Nonadecanone  | 1.37 |
| 16 | 1H-pyrrolo [3,4-b] quinoline-1-one, 2,3-dihydro-7-methyl-2-propyl-3-propylimino | 1.20 |
| 17 | Deccanohydrazide  | 1.15 |

Table shows the result of Gas Chromatography analysis. The GC analysis was only conducted for sample B. Sample B is the one with 30 minutes reaction time. In the graph, there are 17 peaks (Appendix A) indicating that there are 17 different composition in the sample. The bold composition is methyl ester which is bio diesel. From the result obtained, the total percentage of methyl ester is 81.23%. Even though n-butanol is used to react with alcohol in the presence of catalyst ( $H_2SO_4$ ), the bio diesel obtained is methyl ester instead of butyl ester. This is because in the original bio oil, the percentage of methanol is high as shown in the table below. The methanol in the original bio oil has taken part in the reaction. Thus methyl ester is produced.

**Table 5: Chemical Composition of Major Bio Oil Constituents**

| <b>Composition</b>                            | <b>Concentration, wt%</b> |
|---|---------------------------|
| Water   | 23.4                      |
| <b>Methanol Insoluble Solids &amp; Lignin</b> | <b>24.9</b>               |
| Cellubiosan                                   | 1.9                       |
| Glyoxal                                       | 1.9                       |
| Hydroxyacetaldehyde                           | 10.2                      |
| Levogluconan                                  | 6.3                       |
| Formaldehyde                                  | 3.0                       |
| Formic Acid                                   | 3.7                       |
| Acetic Acid                                   | 4.2                       |
| Acetol  | 4.8                       |

#### 4.1.2 Density

**Table 6: Result of Density Analysis**

| <b>Sample</b> | <b>Reaction Time, min</b> | <b>Density, g/ml</b> |
|---------------|---------------------------|----------------------|
| A             | 15                        | 0.9103               |
| B             | 30                        | 0.9235               |

Table 5 shows the result of density analysis. There are two sample which is sample A and sample B. For sample A the reaction time is 15 minutes and for sample B the reaction time is 30 minutes. The density for sample A is 0.9103 g/ml whereas for sample B is 0.9875 g/ml. The density for both samples is approaching the density of water. As stated in the general equation before, the product of esterification will gives bio-diesel, by product and water. Because the final product contains water, this might give effect in the density of the product which is the density approaching the density of water which is 1 g/ml. The different of the density between both samples is quite small even though the reaction time for both samples is different. If the result of the density analysis is compared with the conventional FAME which is 0.88 g/ml, the density for sample A and B are higher.

#### 4.1.2 Water Content

**Table 7 : Result of Water Content Analysis**

| <b>Sample</b> | <b>Reaction Time, min</b> | <b>Volume, mL</b> | <b>Water Content, %</b> |
|---------------|---------------------------|-------------------|-------------------------|
| A             | 15                        | 0.022             | 28.762                  |
| B             | 30                        | 0.019             | 27.131                  |

Table 6 shows the result of water content analysis. For sample A, the volume of the sample tested is 0.022 mL and the result of the water content analysis is 28.762%. for sample B, the volume of the sample tested is 0.018 mL and the result of the water content analysis is 27.131%. As stated in the general equation before, the product of esterification of bio oil and alcohol will give bio diesel, by product and water. The percentage of water content is quite high for both samples. Percentage of water content for sample B is less than sample A due to the longer reaction time for sample B compare to sample A. The water content result for both samples is reduced compare to the

original bio oil which is 30%. From the literature review, this reduction is due to blending with n-butanol as well as due to removal of water by evaporation. If the result of the water content analysis is compared with the conventional FAME which is 0.05 vol%, the percentage of water content for sample A and B are higher.

#### 4.1.2 pH value

**Table 8 : Result of pH Analysis**

| <b>Sample</b> | <b>Reaction Time, min</b> | <b>pH value</b> |
|---------------|---------------------------|-----------------|
| A             | 15                        | 4.333           |
| B             | 30                        | 4.242           |

Table 7 shows the result of pH analysis. For sample A, the reaction time is 15 minutes and the pH value is 4.333. For sample B, the reaction time is 30 minutes and the pH value is 4.242. The pH value for both samples is quite low due to the acidity of the sample itself. From literature review, in the absence of sulphuric acid, the pH of the product is slightly higher than the original bio oil which is 3. This is due to the diluting effect of n-butanol as well as the occurrence of esterification reactions, catalyzed by organic acid present. If the result of the pH value test is compared with the conventional FAME which is 7.0, the pH value for sample A and B are lower.

#### 4.1.2 Viscosity

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

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATION**

#### **5.1 Conclusion**

1. Conversion of bio oil to bio diesel by using reactive distillation column approach produce bio diesel which is methyl ester.
2. The physical properties of the treated bio oil is not as conventional bio diesel. The value of properties is much different in terms of water content, pH value, and Density

#### **5.2 Recommendation**

1. Use the actual volume ratio for the experiment since for this experiment the volume had been downscale
2. Use different type of bio oil since the bio oil used in this experiment is from pyrolysis of palm kernel.

## REFERENCES

Arvinder P. Singh, B. Brian He and Joe C. Thompson, 2004, "A Continuous-flow Reactive Distillation Reactor for Biodiesel Preparation from Seed Oils"

A.Z. Abdullah, B. Salamatinia, H. Mootabadi and S. Bhatia, 2009, "Current status and policies on biodiesel industry in Malaysia as the world's leading producer of palm oil", *Energy Policy*

A. Abdul Aziz, I.M. Atadashi and M.K. Aroua, 2010, "High quality of biodiesel and its diesel engine application : A review", *Renewable and Sustainable Energy Reviews*

F.H. Mahfud, H.J. Heeres, Melian-Cabrera and R. Manurung, 2007, "Upgrading of Flash Pyrolysis Oil by Reactive Distillation Using a High Boiling Alcohol and Acid Catalyst", *Biomass to Fuels*  
IChemE Vol 85(B5)466-472

Gerpen JV, 2005, "Biodiesel processing and production", *Fuel Processing Technology* 86:1097-107.

Hassan MG, Hellgardt C, Gunvachai K, Shama G, 2007, "A new solubility model to describe biodiesel formation kinetics".  
IChemE; 85(B5):383-9.

Hoi W.K and Koh M.P., January 2008, "Issues and Challenges", *Biomass Energy Technology in Malaysia*

<[http://www.researchsea.com/html/article.php/aid/2662/cid/1/research/biomass\\_energy\\_technology\\_in\\_malaysia\\_issues\\_and\\_challenges.html](http://www.researchsea.com/html/article.php/aid/2662/cid/1/research/biomass_energy_technology_in_malaysia_issues_and_challenges.html)>

Juhaini Aittamaa, 1999, "BriteEuram Project Reactive distillation BE95-1335",  
*Synthesis Report*

< <http://www.pollutionissues.com/Na-Ph/Petroleum.html> >

<<http://www.dynamotive.com/industrialfuels/biooil/>>

Puppan D. Environmental evaluation of biofuels. *Periodica Polytechnica Series  
Social and Management Sciences* 2002;10:95–116.

Mohan, Dinesh, Charles U. Pittman and Philip H. Steele, 2006, "Pyrolysis of  
Wood/Biomass for Bio-oil: A Critical Review." *Energy & Fuels*. Vol. 20, No. 3, p. 850.

Mohamed Afiq Bin Ramli, Final Year Project, July 2010

## APENDICES

### Appendice 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  |

$$\log P_{Saturatedapor}^* = A - \frac{B}{T + C}$$

n-butanol;  
At T= 40°C

$$P_{saturatedapor}^* = 10^{(7.2906 - \frac{1282.85}{173.247 + 40})}$$

$$= 18.8290 \text{ mmHg}$$

Table A- 2: Saturated vapor pressure

| T / °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

$$P_{saturatedapor,mixture}^* = \sum P_{saturatedapor,i}^* x_i$$

At T=40°C,

$$P_{saturatedapor}^* = (0.9 \cdot 18.8290) + (0.1 \cdot 22.4685)$$

$$= 19.1929 \text{ mmHg}$$

Table A- 3: Saturated vapor pressure for mixture solution

| T / °C | $p_i x_{butanol}$ | $p_i x_{H_2SO_4}$ | 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 |

## Appendice B

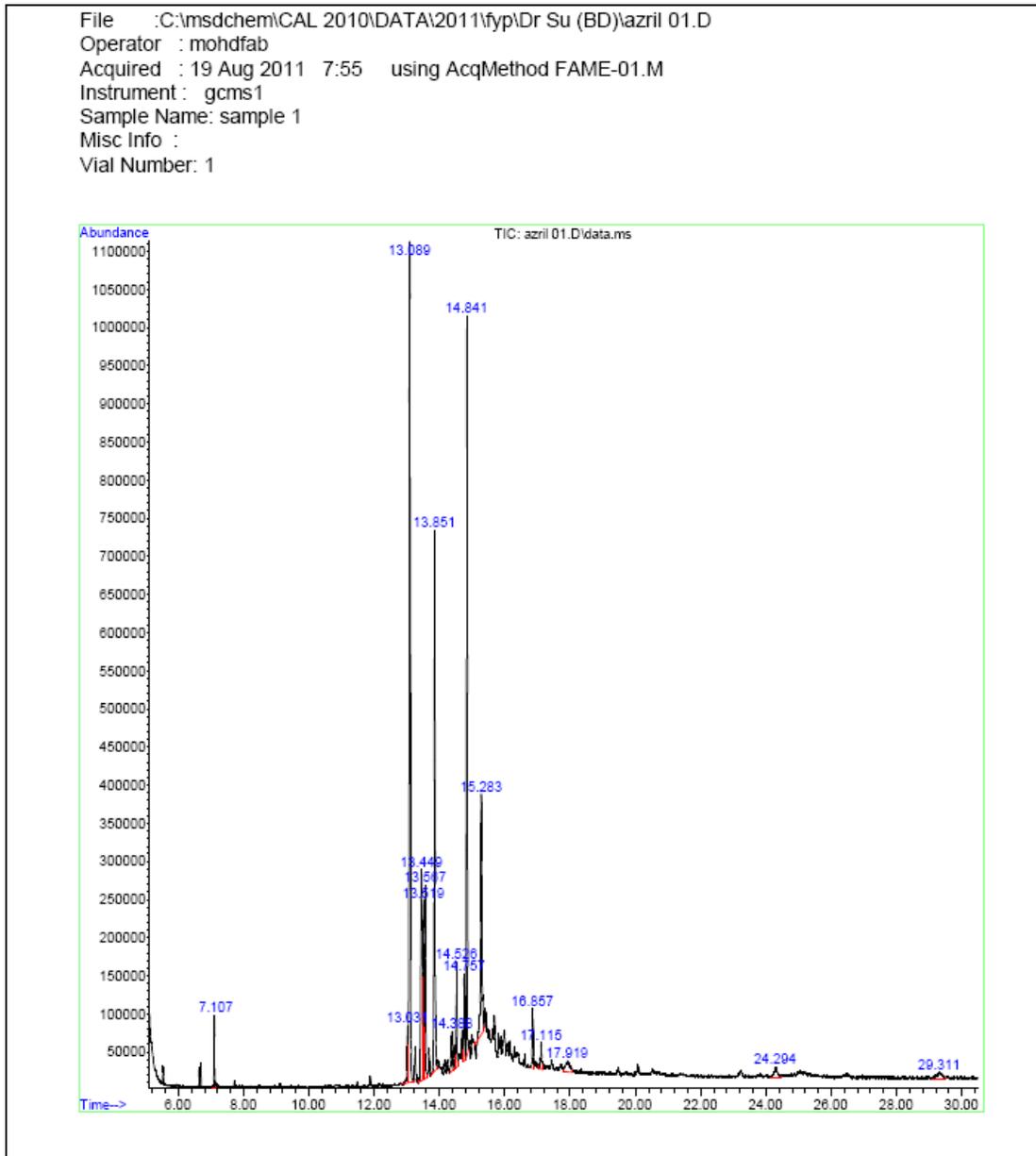


Figure 7 : GC Analysis Peak Result

Area Percent Report

Acq On : 19 Aug 2011 7:55

Sample : sample 1

Data File : azril 01.D

Data Path : C:\msdchem\CAL 2010\DATA\2011\fyp\Dr Su (BD)\

DataAcq Meth:FAME-01.M

Misc :

Operator : mohdfab

Integration Parameters: famel.e

Signal : TIC: azril 01.D\data.ms

| peak # | R.T. min | first scan | max scan | last scan | PK TY | peak height | corr. area | corr. % max. | % of total |
|--------|----------|------------|----------|-----------|-------|-------------|------------|--------------|------------|
| 1      | 7.107    | 376        | 389      | 400       | VV    | 92242       | 1127014    | 4.78%        | 1.166%     |
| 2      | 13.031   | 1499       | 1531     | 1534      | BV 4  | 74618       | 1519681    | 6.45%        | 1.573%     |
| 3      | 13.089   | 1534       | 1542     | 1563      | VB 2  | 1095519     | 23566323   | 100.00%      | 24.388%    |
| 4      | 13.449   | 1590       | 1612     | 1621      | BV 3  | 276301      | 9679484    | 41.07%       | 10.017%    |
| 5      | 13.519   | 1621       | 1625     | 1630      | VV    | 231206      | 4490875    | 19.06%       | 4.647%     |
| 6      | 13.567   | 1630       | 1634     | 1646      | VV    | 249031      | 4522439    | 19.19%       | 4.680%     |
| 7      | 13.851   | 1667       | 1689     | 1706      | PV 2  | 704471      | 13827806   | 58.68%       | 14.310%    |
| 8      | 14.388   | 1777       | 1793     | 1799      | BV 10 | 51088       | 1581580    | 6.71%        | 1.637%     |
| 9      | 14.526   | 1810       | 1819     | 1826      | VV 3  | 137337      | 2694573    | 11.43%       | 2.789%     |
| 10     | 14.757   | 1858       | 1864     | 1871      | VV 2  | 113154      | 2123250    | 9.01%        | 2.197%     |
| 11     | 14.841   | 1871       | 1880     | 1889      | PV 2  | 972325      | 16576591   | 70.34%       | 17.154%    |
| 12     | 15.283   | 1924       | 1965     | 1981      | BV 4  | 314523      | 8482412    | 35.99%       | 8.778%     |
| 13     | 16.857   | 2259       | 2269     | 2277      | VV 2  | 78302       | 1722149    | 7.31%        | 1.782%     |
| 14     | 17.115   | 2299       | 2318     | 2329      | VV 4  | 33542       | 1122476    | 4.76%        | 1.162%     |
| 15     | 17.919   | 2452       | 2473     | 2504      | VV 4  | 14497       | 1324521    | 5.62%        | 1.371%     |
| 16     | 24.294   | 3671       | 3702     | 3732      | VV 4  | 13641       | 1161348    | 4.93%        | 1.202%     |
| 17     | 29.311   | 4629       | 4669     | 4704      | VV 4  | 8821        | 1108994    | 4.71%        | 1.148%     |

Sum of corrected areas: 96631516

FAME-01.M Fri Aug 19 08:51:36 2011

**Figure 8 : GC Analysis (Area Percent)**