CERTIFICATION OF APPROVAL

The Solubility Behavior during Transesterification Of Triglyceride

By

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Approved by,

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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.

MOHD SAIFUL BIN MOHD SOFIAN

ABSTRACT

Biodiesel had been studied to be used as the additional source of diesel as to cater the depletion of fossil fuel, especially in the diesel derives from the crude oil. Biodiesel is the common name for the fatty acid methyl ester (FAME) that produced through the Transesterification process of triglyceride and methanol. The first biodiesel was introduced since the early of 1900 and many researches had been done to improve the production of biodiesel including by looking at many sources of triglyceride. As in Malaysia, the easiest source of triglyceride is the palm oil and it is abundant here. The problem with the biodiesel production is that the miscibility between the palm oil and methanol that leads to the reaction. This is because, both components are immiscible again one another. So, the exact reaction location is still not convincingly identified yet. In this project, there were three experimental works had been done to answer the doubt about the reaction location. From the experimental works, the location of the reaction was inside the methanol rich phase whiles the present of FAME is the dispersion factor for the palm cooking oil into the methanol rich phase.

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CHAPTER 1

INTRODUCTION

Palm oil having the characteristic almost similar as diesel derived from crude oil for diesel engine. However, the ordinary palm oil cannot be used directly for the diesel engine because of the limitation onto the characteristic of the palm oil such as the viscosity. The viscosity of the palm oil is much higher compared to the ordinary diesel. This will be a problem for the engine to start. These difficulties however can be reduced by using the biodiesel as a blend to the current fossil diesel.

Biodiesel is produced by converting the triglyceride inside the palm oil into fatty acid methyl ester (FAME) through the Transesterification process. In this process, the triglyceride will react with methanol in the present of potassium hydroxide or sodium hydroxide as the catalyst to produce FAME and glycerol as the byproduct. The main component that actually labeled as the biodiesel is the FAME.

In this process, 1mole of triglyceride from the vegetable oil will reacted with 3 mole of methanol in the present of catalyst which the potassium hydroxide to produce 1 mole of fatty acid methyl ester (FAME) and 3mole of glycerol.

$$\mathrm{TRIGLYCERIDE + METHANOL \xleftrightarrow{CATALYST} METHYL\ ESTER + DIGLYCERIDE}$$

$$\mathrm{DIGLYCERIDE + METHANOL \xleftrightarrow{CATALYST} METHYL\ ESTER\ + MONOGLYCERIDE}$$

$$\mathrm{MONOGLYCERIDE + METHANOL \xleftrightarrow{CATALYST} METHYL\ ESTER + GLYCEROL}$$

The production of biodiesel is present since 1900s. But until now, no concrete study had been made about the reaction phase during the Transesterification process of biodiesel. There are conflicting between several researchers about the exact reaction location. Some of them said the reaction happens as the inter-phase between palm oil and the methanol, some of them said that the reaction happens inside the methanol phase and some of them said that the reaction happens at the present of another component which FAME.

1.1 Problem Statement

When we mix the palm cooking oil and the methanol at the initial phase of the process, we will have 2 clear separate phases of liquid. This is due to the different on polarity for both reactants. Palm oil is a non-polar component while methanol is a polar component. Due to this, both components are hardly miscible each other. But still, we will identify that the reaction between the components follow the normal trend as any other reaction process. This means that there are regions which the reaction rate is high and the regions which the reaction rate is low. As the project supervisor is concerned, there is no paper work or research had been made to show the region which the reaction is happens. The identification of the reaction area is important because according to Matthew Slinn and Kevin Kendall (2008) the reaction to produce biodiesel is not determined by the thermodynamics of the reaction, but is determined by either the kinetics rate or the mass transfer. This shows that how crucial the understanding of the mass transfer in the biodiesel making process. The manipulation of the mass transfer hopefully later can bring the biodiesel making process another step further.

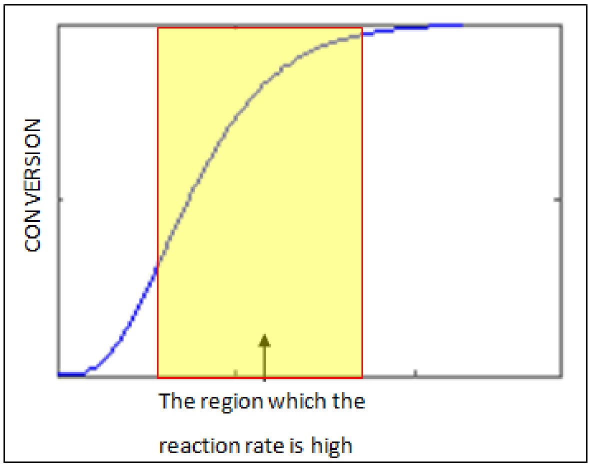


Figure 1: The region which the reaction rate is high

In the journal of Applied Energy title "A Review on Biodiesel Production Using Catalyzed Transesterification" by Dennis Y.C. Leung *et al.*, 2009 claim that the contact surface between the vegetable oil and the methanol will be the determining factor for the reaction to occur. In order to increase the reaction rate, the contact surface between vegetable oil and methanol should be increase. By saying this, they believe to agitate the mixture to form the emulsions as the surface area will be more.

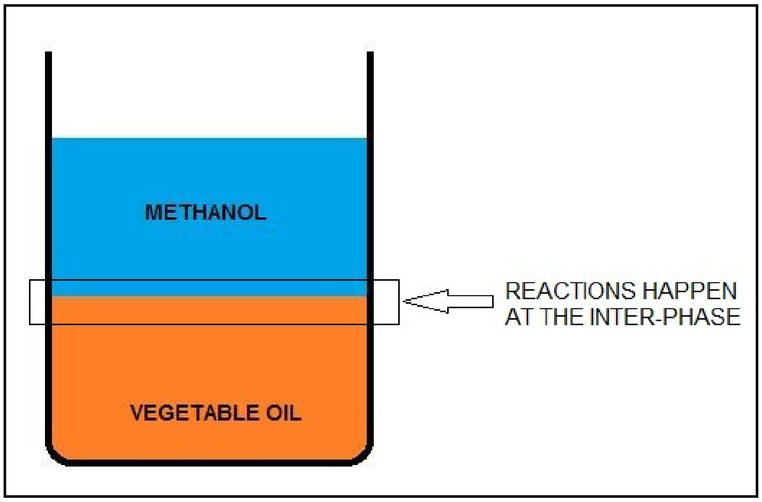


Figure 2: Initial assumption about the reaction

Also, there are papers indicate that, the reaction is actually happens in the methanol phase. K. Gunvachai *et al.* (2007) in the journal title “A new solubility model to describe biodiesel formation kinetics” performing mathematical calculation using the correlation factor proposed by Selker and Sleicher (1995) and the finding indicate that the reaction happens in the region which falls into the methanol phase.

From the correlation factor calculation, they found that the methanol is dispersed in a continuous phase of oil. This is because the solubility between the catalyst and the methanol will carry the reaction. Also, the formation of the FAME increases the solubility of vegetable oil into the methanol. This was confirmed by referring to the correlation table as below.

But, in the other hand, Jon Van Gerpen (2005) indicates that the reaction happens in the vegetable oil phase. In His paper, he stated that, in the initial phase of the reaction, the conversion is low due to the limitation which the amount of methanol present in the oil is low. He refers to Boocock that proposed the introduction of co-solvent that will increase the solubility thus make the solution into a single phase.

By highlighting these 3 conflict statement made by researchers before, the direction of this project is to make clear the actual situation where is the reaction is actually happens by study the solubility between the components the present during the biodiesel making process. As indicate at the initial part of the statement, the key factor that determines the conversion of the reactant is the mass transfer. At the end of this project, the outcome is to identify the actual situation which the reaction is actually happens. With this, future project can be planned to manipulate the outcome so that the production of biodiesel can be brought to another level higher.

1.2 Objectives

There are several objectives aimed for this project. All these objectives will be the main focus in designing the experimental works. This research work purposely to clarify few things related to the biodiesel reaction;

1. To produce a laboratory scale biodiesel that meet standard specification. This biodiesel will be tested for the purity of the FAME content. Since the produced biodiesel will be used in further experimental works, the requirement for the biodiesel to meet the standard is important. The purity content of biodiesel is tested with the European Standard for Biodiesel (B100), EN14214.
2. To study the solubility and phase behavior of the four components system involved during Transesterification reaction to produce biodiesel (methanol, fatty acid methyl ester (FAME), triglyceride and glycerol). This is because, we need to identify the solubility between the components and to find the probable factor that governing the solubility behavior.
3. To find the exact location of the reaction takes place. This is to identify the accurate argument made by the three researchers before.

For this research work, the source of triglyceride will be the palm cooking oil. This is because to suit the Malaysia condition that having large amount of palm oil. Also, the amount of fatty acid inside the palm cooking oil is high (at about 50%) (S. Baroutian et. al).

1.3 Scope of Study

Few initial experimental works had been identified and carried out which are:

- Experimental works to produce the biodiesel using the conventional technique. This biodiesel later used as the component for later stage of the project.
- Initial experiment to identify the solubility between the components in biodiesel making process (palm oil, methanol, FAME and glycerol).
- After the initial experiment, the solubility experiment further carried out in longer period of time and more detail analysis.

Upon completing the initial experiment, which the solubility behavior of the biodiesel reaction process, the research will focus into the design of the membrane reactor for trans-esterification process. The data obtained from the solubility experiment will determine the size of the membrane that suitable to be used as for the reaction to happens in small scale membrane reactor.

CHAPTER 2

LITERATURE REVIEW

As for the early part of the experimental works, the project begins with preparing the biodiesel that will be used throughout the project. For this purpose, the parameters of the experiment basically obtained from the literature review. The biodiesel produced was tested for the purity of FAME content as according to the standard. All the parameters for this first experiment basically based on the literature review study that performed before.

According to Jon Van Garpen (2005), the most suitable temperature for biodiesel reaction is at 60^{o}C. Since the reaction is an exothermic reaction, it is applicable to have a temperature that higher than at room temperature. He also compares the effect of temperature at biodiesel reaction at which, the reaction complete faster at higher temperature.

The suitable vegetable oil or vegetable oil can be used as the feedstock for the reaction. The selection of the feedstock basically based on the economic and chemical factors. As to meet the local scenario, palm cooking oil had been used as the feedstock and the source of triglyceride. The palm cooking oil is largely available in Malaysia and the triglyceride content inside the oil is more than 50% (S. Baroutian *et. al.,* 2009).

The proposed ratio between methanol and palm oil also had been discussed. Small amount of ratio will give incomplete reaction which is not favored. This is because the reactions are reversible. The proposed methanol to vegetable oil ratio is 6:1. Also, in most of the literature survey, the amount of methanol that been used for the experiment is at 300 mol% excess than the proposed ratio. This is to make sure the reaction is complete and suppressed forward as the reaction occurs. The excess amount of methanol is also the current practice in the industry.

The role of catalyst also been discussed by the author. He explain how the effect of catalyst into the reaction which reduce the amount of ratio between methanol into vegetable oil. The catalyst that suitable for this reaction is the sodium hydroxide (NaOH) or potassium hydroxide (KOH). But, with the present of catalyst into the reaction, the product needs to be 'washed' to remove the catalyst. In the paper, the proposed amount of catalyst is 5 wt% based on vegetable oil. The biodiesel is later tested for the purity of FAME and was compared to the European Standard for biodiesel (EN 14214).

Table 1. Specification for biodiesel (B100) - EN14214

PROPERTY	TESTING METHOD	LIMITS		UNIT
		LOWER	UPPER	
Ester content	EN 14103	96.5		% (m/m)
Density (15°c)	EN ISO 3675	860	900	kg/m^3
Viscosity (40°C)	EN ISO 3104	3.5	5	mm²/s
Flash point	EN ISO 3679	120		°C
Sulfur content	EN ISO 20846		10	mg/kg
Carbon residue	EN ISO 10370		0.3	% (m/m)
Cetane number	EN ISO 5165	51		
Sulfur ash content	ISO 3987		0.02	% (m/m)
Water content	EN ISO 12937		500	mg/kg
Total contamination	EN 12662		24	mg/kg
Oxidation stability (110°C)	EN 14112	6		h
Acid value	EN 14104		0.5	mg KOH/g
Iodine value	EN 14111		120	g iodine/100g
Linolic acid methyl ester	EN 14103		12	% (m/m)
Methanol content	EN 14110		0.2	% (m/m)
Monoglyceride content	EN 14105		0.8	% (m/m)
Diglyceride content	EN 14105		0.2	% (m/m)
Triglyceride content	EN 14105		0.2	% (m/m)
Free glycerol	EN 14105		0.02	% (m/m)
Total glycerol	EN 14105		0.25	% (m/m)
Alkaline metal (Na+K)	EN 14108		5	mg/kg
Alkaline earth metal (Ca+Mg)	prEN 14538		5	mg/kg
Phosphorus content	EN 14107		10	mg/kg

Further analysis of the project objective is done. The problems arise regarding the actual location of the reaction is further investigated by referring to 3 separate journals. First, Denning Y.C. Leung *et. al.* (2009) report that, the reaction between methanol and vegetable oil happens in the inter-phase region. This is the region where methanol phase and vegetable oil phase are met. The author performs the experiment by using the agitated vessel which means to increase the surface contact between vegetable oil and methanol. Prior to his experiment, the author believes that the phase boundary can be reduce by introducing cavitations of bubbles using ultrasonic can further increase the reaction rate.

In another journal, Jon Van Gerpen (2005) highlight that, the reaction is happens at the vegetable oil phase. The reaction is slow at the initial phase because the amount of methanol inside the vegetable oil is small. The author also believe the introduction of co solvent that will further bring the reactant into a single phase. Which is can lead to higher reaction rate as the contact surface between vegetable oil and methanol is higher.

Meanwhile K. Gunvacai *et. al.,* (2007) propose the using of correlation factor to identify the component that is dispersed in biodiesel reaction process. The author using a mathematical calculation to pin point the location at which the reaction happens. The calculation first developed by Selker and Sleicher (1995).

$$X = \frac{Q_L}{Q_H}\left(\frac{\rho_L \mu_L}{\rho_H \mu_H}\right)^{0.3}$$

Q_L=volume of light component
Q_H=volume of heavy component
ρ_L=density of light component
ρ_H=density of heavy component
μ_L=viscosity of light component
μ_H=viscosity of heavy component

Light component is methanol (density 791.8 kg/m^3 at 25^{o}C).
Heavy component is vegetable oil (density 907 kg/m^3 at 25^{o}C).

By using the correlation factor, the location of the reaction can be determined by referring to the table below.

Table2. Relationship between dispersion types and values of the correlation factor

Correlation Factor, X	Results
<0.3	Light phase always dispersed
0.3-0.5	Light phase probably dispersed
0.5-2.0	Phase inversion possible
2.0-3.3	Heavy phase probably dispersed
>3.3	Heavy phase always dispersed

From this equation, the author found that the methanol is **dispersed** in a continuous phase of oil which can be seen that the reaction is happens in the methanol as indicated in the journal.

CHAPTER 3

METHODOLOGY AND PROJECT WORK

There are several experimental processes involved in this project. All this experiments were conducted in a way to achieve the final objective of this project. There are about four experimental works were conducted in this project to achieve the goal. Based on the literature study, the chemicals and parameters for the experiment as below.

List of chemicals: Palm cooking oil oil, Methanol, Potassium hydroxide, glycerol, M-Methyl-N-trimethylsilyltrifluoracetamide (MSTFA), tricaprin, n-Heptane.

The palm cooking oil that been used in this project is the refined, bleached and deodorized (RBD) commercial grade palm cooking oil 'Vesawit' that was purchased from the local market. The properties of the palm cooking oil as in table below:

Table 3: Properties of Vesawit brand palm cooking oil.

Fatty acid contents	: Less than 0.1% (as palmitic acid)
Saponification value	: 194-202 mg KOH
Iodine value	: Not less than 56
Melting point	: Not more than 24 °C
Density	: 0.907 g/cm3

Data taken from A. Farizul et. al.

List of apparatus: Magnetic stirrer with hot plate, beaker, scale, separator flask, thermometer, and gas chromatograph analyzer.

In general, the experiment is conducted at the conversion stage of 10%, 20%, 50%, 70% and 90%. At particular stage, the reaction is quenched by eliminating the catalyst (potassium hydroxide) from the materials. All for sets of experiment was done at specified conversion and their result was taken. The four experiments were:

3.1 Biodiesel Making Experiment.

Biodiesel can be produced through Transesterification process using fatty acids called triglyceride to react with alcohol in the present of catalyst to produce FAME and glycerol (Dennis Y.C. Leung *et. al.*, 2010). The cooking palm oil that been used in this experiment is the refined palm oil that available in the market, methanol as for alcohol and the potassium hydroxide for the catalyst. The molar ratio of methanol to palm oil is 6:1 (Jon Van Gerpen, 2005). The amount of catalyst used in this experiment was 5 wt% based on the amount of palm oil. In total, the amounts of the chemical used in this experiment were 200 grams of palm oil, 70.73 grams of methanol and 3.54 grams of potassium hydroxide.

The experiment begins with the mixing process between methanol and potassium hydroxide in a 500 mL beaker. The mixture went through the stirring process until all the potassium hydroxide dissolved into the methanol. These steps begin as to avoid the reaction of fatty with catalyst that will give the formation of soap through saponification (Dennis Y.C. Leung *et. al.,* 2010). This reaction is not favored as this will reduce the yield of biodiesel product. The mixture of methanol and potassium hydroxide will produce potassium methoxide.

The palm cooking oil will be pre-heated to the temperature of 60^{o}C as the preparation for the reaction inside a 500 mL beaker. The heating process takes place at a magnetic stirrer with the hot plate. The speed of the stirrer was set to 3000 rpm. The temperature of the palm cooking oil is monitored by using the thermometer every 10 seconds until the temperature reach 60 ^{o}C. This is because the reaction is an endothermic reaction. The potassium methoxide that prepared earlier was added into the heated palm oil and the mixture went through the stirring process for 10 minutes. The time takes is necessary to achieve a complete reaction (K. Gunvachai *et. al.,* 2007). The product was left to settle down for 20 minutes. The upper part of the product mainly consists of FAME and the bottom part consist the glycerol. After 20 minutes, the products were put into the separator funnel to separate FAME and the glycerol and let to settle down. After we have 2 clear immiscible boundaries, the solutions are separated into different beaker. The upper part before that mainly FAME will go to further purification with the elimination of the catalyst and the methanol inside.

It will go through the ‘washing’ process (Z. Helwani *et. al.,* 2009) where equal amount of distilled water and FAME were added together in a 1 liter beaker. The mixtures then were stirred for 10 minutes in a magnetic stirrer and left to settle down for 30 minutes. The mixtures were then transferred into a separator funnel and left to settle down. The upper part is the FAME and the bottom part is the wastewater. The two boundary solutions were separated into different beaker and the wastewater was tested with pH meter and the reading is recorded. The process was repeated (Z. Helwani *et. al.,* 2009) until the pH reading indicates the wastewater is neutral.

The sample of the FAME was sent for gas chromatograph analysis (GC-MS) to identify whether the purity of FAME produce met the standard or not since the FAME is used for further experiments.

3.2 Preliminary Solubility Experiment.

This experiment was conducted for the purpose to identify the solubility behavior between all the components involved in biodiesel reaction. Those components were palm oil, methanol, FAME and glycerol. The catalyst, potassium hydroxide was not present in this experiment since the experiment was conducted in a way that to stop the reaction from happening. By eliminating the catalyst, the reaction will happens at a very slow rate and taking very long time to complete. By applying this, the situation as the given conversion can be simulated and the reaction can be quenched.

The experiment was conducted in three different level of conversion which at 0%, 10%, and 20%.The conversions calculation was starting on the mol of palm oil and methanol present at the 0% conversion. At 0% conversion, the amount of palm oil used was 32 grams and methanol was 17.01 grams (1.5 times excess). From there, the calculations for later stage of conversion were made in the stoichiometry of 1mol of fatty acid react with 3mol of methanol to produce 3mol of FAME and 1mol of glycerol.

The details of the amount of each components been used in this experiment are available in the table below.

Table 4: The amount of each component had been used in experiment 2.

Run	Conversion level (%)	Amount of palm oil (g)	Amount of Methanol (g)	Amount of FAME (g)	Amount of glycerol (g)
A	0	32.00	17.01	0	0
B	10	28.80	15.31	3.81	1.09
C	20	25.60	13.61	7.63	2.17

For every run, the components were weight on a weight scale and added together according to the specified weight at the given conversion inside a 250 mL beaker. The mixtures were stirred for 10 minutes on a magnetic stirrer with the stirring speed of 3000 rpm and then left to settle down for 10 minutes. The number of phases present in each conversion was observed and recorded. The sample then was transferred into the separator funnel. The phases were separated into their part and the weights of the each phase were recorded.

3.3 Detail Solubility Experiment

Prior to the result obtained in previous experiment, the detail experiment to study the solubility behavior of each component was conducted. In this experiment, modification was made to the time for the stirring process which from 10 minutes to 1 hour. With longer time for the mixing process, the components having a longer time to miscible inside each other and the effect will be clearer. From the result in previous experiment, the number of phases present does not according to the understanding.

Most of the other parameters for the experiment were remaining the same as the previous experiment. Except for few modifications as according to the literature study that performed after the first experiment. First, modifications were made to the amount of methanol used in this experiment. Previously, the amount of methanol used just in the excess of 1.5 times, but in this experiment, the amount of methanol used was in the excess of 300% or 3 times in the molar amount, while the conversion level also further increased to 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% of conversion level. The detail amount for every component in every runs as according to the table below.

Table 5: The amount of each component had been used in experiment 3.

Run	Conversion level (%)	Amount of palm oil (g)	Amount of Methanol (g) [300mol% excess]	Amount of FAME (g)	Amount of glycerol (g)
A	10	26.90	30.66	3.13	1.01
B	20	23.90	29.60	6.17	2.03
C	30	20.9	28.54	9.22	3.04
D	40	17.9	27.49	12.26	4.05
E	50	14.95	26.43	15.26	5.07
F	60	11.96	25.37	18.29	6.08
G	70	8.97	24.31	21.33	7.09
H	80	5.98	23.27	24.35	8.10
I	90	2.99	22.20	27.39	9.12

Similar in the previous experiment, the components were weight according to the specified amount in every run and were mixed together in a 500 mL beaker. The sample then was let to stirring process at the stirring speed of 3000 rpm and at room temperature for 1 hour. The mixture then were left to settle for 10 minutes before were transferred into the separator funnel. The mixture were then separated into each phases and been weight. The results were recorded.

Further improvement in this experiment is that the sample taken from each phases for every run and sent for *Gas Chromatograph with Flame Ionization Detector* (GC-FID) analysis. The samples were from the *Run A* and the *Run I* as the particular runs representing the early stage of the reaction and also the final stage of the reaction.

3.4 Optical Observation Experiment

The main objective in this experiment is to determine the solubility behavior of the components during the biodiesel reaction. The experiment was done through the optical observation as to see wish component is dispersed in which component during the reaction at different level of conversions.

Similar to the previous experiments, the experiment was carried out the different levels of conversion which at 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% conversion level. These level of conversions were achieved by measuring the amount of each components present during the specified conversion level. The calculation of the amount basically was based on the molar amount that the component should have during the specified level.

Table 6: The amount of each component had been used in experiment 4.

Run	Conversion level (%)	Amount of palm oil (g)	Amount of Methanol (g) [300mol% excess]	Amount of FAME (g)	Amount of glycerol (g)
A	10	26.90	30.66	3.13	1.01
B	20	23.90	29.60	6.17	2.03
C	30	20.9	28.54	9.22	3.04
D	40	17.9	27.49	12.26	4.05
E	50	14.95	26.43	15.26	5.07
F	60	11.96	25.37	18.29	6.08
G	70	8.97	24.31	21.33	7.09
H	80	5.98	23.27	24.35	8.10
I	90	2.99	22.20	27.39	9.12

In this experiment, the methanol that been used was first prepared. 500 mL of methanol were added with 5 g of green water soluble dye in a 1 L beaker. This is to differentiate between the methanol and the other phases during the experiment.

The pictures of the setting process were taken using digital camera brand *'Ricoh'* model CX4 with the setting interval time of 5 seconds between every picture taken. The setup of the distance between the camera and the beaker was set at 40 cm apart.

Similar in the previous experiment, the components were weight according to the specified amount in every run and were mixed together in a 500 mL beaker. The sample then was left to stirring process at the stirring speed of 300 rpm for 10 minutes. Once the stirring process was stop, the camera will start to capture the picture of the mixture at every 5 seconds until the mixture completely settle. The mixture was considered as settle when there is no droplet formed at the inter-phase between the phases present.

CHAPTER 4

SAMPLE ANALYSIS

For the determination of the FAME purity in the experiment number 1, the sample of the FAME was analyzed using the gas chromatograph analyzer with flame ionization detector (GC-MS). The equipment is used to identify the component present in the FAME product together with the purity of each component inside. In the experiment number 3, the products are analyzed by Gas Chromatography with FID using 30m x 0.32 mm ID x 0.1 μm film thickness, SHMADZU GC 2010 with SGE HT-5.Analysis conditions for all reactants and products are set to be the same so that comparison can easily be made. The analysis conditions are set as follows;

Oven Temperature: 50 ℃
Detector Temperature: FID 385 ℃
Injection temperature: On column injection, 380 ℃
Carrier gas: Nitrogen

CHAPTER 5

RESULT AND DISCUSSION

5.1 Experiment 1: Biodiesel Making Experiment

After separation, the FAME rich phase will undergo the washing process, the purpose of this washing process is to eliminate the catalyst (sodium hydroxide) and some amount of methanol in the FAME phase. The pH reading of the water from the washing process was taken to identify whether the catalyst had been remove from the FAME rich phase.

Table 7: The pH number of the wastewater from the washing process.

Run	pH reading
1	10.57
2	9.80
3	8.50
4	7.53

From the table, we can see that as the number of run increases, the pH reading of the water started to reduce. Since the catalyst, potassium hydroxide is a basic compound, the reading of the pH meter should be in the region from 7 to 14. The higher the number, the more basic the FAME product would be. As in the table 6 above, as the number of water cycle introduced into the FAME, the pH meter reading started to decrease. This is because, the amount of potassium hydroxide inside the FAME rich phase started to decrease.

From the GC-MS analysis, the amount of impurities present in the FAME product can be determined.

Table 8: The impurities content inside the biodiesel product

Compound Name	**Concentration (µg)**
Glycerine	14.39255
Monoglyceride	198.71864
Diglyceride	166.90459
Triglyceride	49.70788
Total	429.72366

By using the equation:

$$\text{Purity} = \frac{\text{amount of sample} - \text{amount of impurity}}{\text{amount of sample}} \text{ X } 100\%$$

$$\text{Purity} = 99.75\%$$

From the result the purity of the FAME produce is more than 99%. The purity of the biodiesel produced is enough to exceed the requirement for the European standard for B100 biodiesel which 96.5% purity of FAME content in the biodiesel. This biodiesel is met the requirement and can be used as the source of FAME in the all other experimental works.

5.2 Experiment 2: Preliminary Solubility Experiment

The number of the phases present after the settling process was recorded and the weight of each phase also were recorded after the separation as according to each phase. The result of the experiment as according to table below.

Table 9: Result for preliminary solubility experiment

Number	INITIAL MASS (g)				Observation	Weight of each phase (g)
	Palm Oil	Methanol	FAME	Glycerol		
A (0%)	32.04	17.00	0.00	0.00	2 Phases	Top: 16.01 Bottom: 33.00
B (10%)	28.80	15.32	3.91	1.10	3 Phases	Top: 14.36 Middle: 32.21 Bottom: 0.62
C (20%)	25.65	13.61	7.63	2.18	3 Phases	Top: 11.89 Middle: 33.91 Bottom: 1.83

From the table, we can see that at the first run of the experiment, the mixing palm oil and methanol exhibit 2 phases solution. This is because the methanol and palm oil are not miscible again each other. This is due to the polarity. Methanol is at polar solution while palm cooking oil is at non-polar solution. Thus, we can easily having two clear phases that immiscible again each other. The upper part of the solution should be methanol while at the bottom part should be palm cooking oil. The determination of the location of the component is due to the density of the component. Palm cooking oil has higher density (970 kg/m^3) compared to the methanol (790 kg/m^3).

In the run number B and C, some amount of FAME and glycerol were introduced into the solution as to represent the reaction that happens at 10% and also 20% conversion. Significantly, four components were introduced finally give just three components as the end. The explanation for this reason is that FAME is miscible into the palm cooking oil phase and not in the methanol phase, while glycerol should miscible into the methanol phase. But, the solubility of glycerol into the methanol should take some time as the polarity of glycerol is low due to the carbon chain in the glycerol. From the final weight of the phases, we can still see that the methanol present as the top of the solution, palm oil with FAME at the middle while at the bottom as should be glycerol. This is because, the density of glycerol is higher (1260 kg/m^3).

Even though the density of glycerol is highest among all, but the amount of the glycerol miscible into the methanol at the very short time is still small that still left methanol at the above of the solution. Fame with density of 870 kg/m^3 still present in a small amount in the palm cooking oil part which let the density of the palm cooking oil to dominate the density to be higher than the methanol part.

5.3 Experiment 3: Detail Solubility Experiment

The number of the phases present after the settling process was recorded and the weight of each phase also were recorded after the separation as according to each phase. The results of the experiment as according to table below.

Table 10: Result for detail solubility experiment

Number	INITIAL MASS (g)				Observation	Weight of each phase (g)
	Palm Oil	Methanol	FAME	Glycerol		
A	26.9	30.66	3.13	1.01	2 Phases	Top:29.93 Bottom:29.61
B	23.9	29.6	6.17	2.03	2 Phases	Top:29.98 Bottom:28.95
C	20.9	28.54	9.22	3.04	2 Phases	Top:30.03 Bottom:28.86
D	17.9	27.49	12.26	4.05	2 Phases	Top:30.15 Bottom:28.78
E	14.95	26.43	15.26	5.07	2 Phases	Top:30.19 Bottom:28.25
F	11.96	25.37	18.29	6.08	2 Phases	Top:30.25 Bottom:28.73
G	8.97	24.31	21.33	7.09	2 Phases	Top:31.42 Bottom: 27.4
H	5.98	23.27	24.35	8.10	2 Phases	Top:31.40 Bottom:28.95
I	2.99	22.2	27.39	9.12	2 Phases	Top:31.25 Bottom:27.57

As compared to the result obtained from the preliminary experiment, the mixing of all components at every level of conversion give out only 2 phases of immiscible liquid. This is because as the understanding before, the glycerol is not completely miscible into the methanol phase at a short period of time. So, as the stirring time of the solutions increases, we can finally having only two clear immiscible phase, eliminating the present of glycerol phase when the total amount of glycerol miscible into the methanol part. Also, in this experiment we can confirm that that the FAME is miscible into the palm cooking oil phase because, the FAME is non-polar component together with the cooking oil, so, the solubility of FAME into the methanol is not happen.

At the initial part of the experiment from 10% until 60% conversion, the upper part of the two clear immiscible solution should be methanol, similar to the previous experiment, the methanol present as the upper part because of the density of methanol is lower than the density of the palm cooking oil. Even though the glycerol with higher density introduced and miscible into the methanol phase, the amount of the glycerol still small compared to the amount of methanol. So, the density of methanol dominates the density of the upper part which gives the place the component in the above part in the solution. But, as the conversion gets higher, the amount of glycerol introduced in the system increases. So, the density of the methanol rich phase had been influenced by the density of the glycerol. So, at the region of 70% to 90% of conversion, the methanol rich side stated to settle at the bottom rather than the upper part. As at 90% conversion, the amount of glycerol introduced into the system is approximately 50% by weight to the methanol. So, the density of glycerol had dominated the methanol rich side.

At higher conversion also, we have the FAME rich side coming to the upper part of the solution. This is because, the density FAME is lower as compared to the density of methanol mixed with glycerol. So, the FAME rich side will appear at the above part of the solution.

But as stated by K. Gunvachai *et. al.* (2007) in their correlation calculation, the palm cooking oil is miscible into the methanol rich component. From the observation of the experiment, the submission of palm cooking oil together with the FAME that miscible into the palm cooking oil that appear at the bottom at the end of settling time at lower conversion is always below than the submission of both components at the initial run of the experiment. From here, we can made early hypothesis that the correlation calculation that had been made can be proven correct. Also, as the amount of FAME introduced into the system increases at higher conversion, the amount of palm cooking oil together with FAME that coming into the methanol rich phase had increased.

5.4 Experiment 4: Optical Observation Experiment

Prior to optical experiment, the result obtained to identify the settling time taken at the given conversion, to identify the arrangement of the phases after settling process and also to observe the behavior of each phases.

As for the first result, the time taken for the mixture to settle after mixing process was taken on the table below:

Table 11: The time taken for settling process.

CONVERSION (%)	SETTLING TIME (seconds)			COLOR ARRANGEMENT
	1	2	Average	
10	95	105	100	Top: **GREEN** Bottom: **YELLOW**
20	105	105	105	Top: **GREEN** Bottom: **YELLOW**
30	125	125	125	Top: **GREEN** Bottom: **YELLOW**
40	140	130	135	Top: **GREEN** Bottom: **YELLOW**
50	130	135	132.5	Top: **GREEN** Bottom: **YELLOW**
60	255	250	252.5	Top: **GREEN** Bottom: **YELLOW**
70	530	520	525	Top: **YELLOW** Bottom: **GREEN**
80	160	155	157.5	Top: **YELLOW** Bottom: **GREEN**
90	80	85	82.5	Top: **YELLOW** Bottom: **GREEN**

Table 12: The image for settling process every 20 seconds at 10%, 20% and 30% conversion.

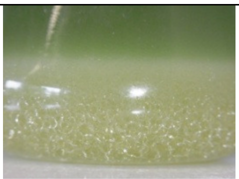
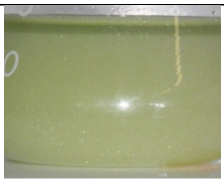
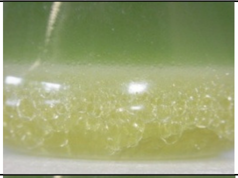
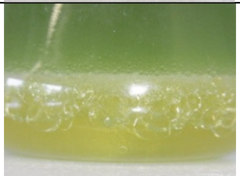
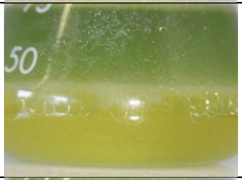
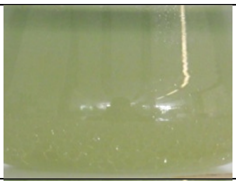
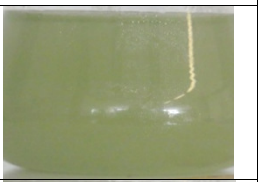
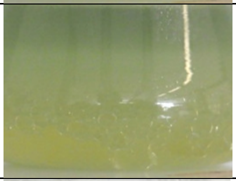
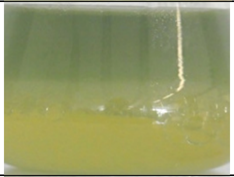
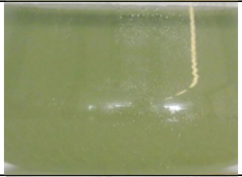
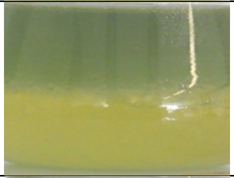
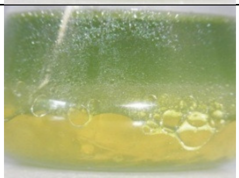
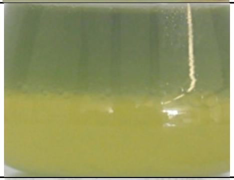
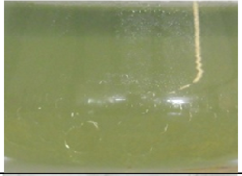
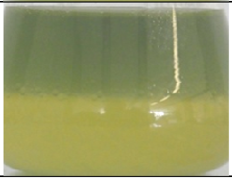
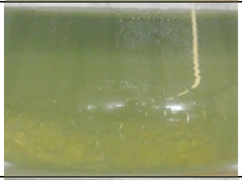
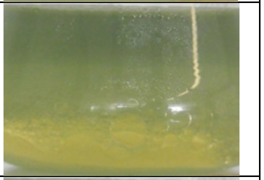
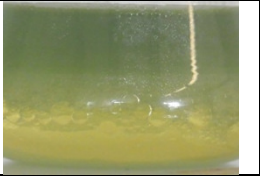
TIME (S)	CONVERSION (%)		
	10	20	30
20			
40			
60			
80			
100			
120			

Table 13: The image for settling process every 20 seconds at 40%, 50% and 60% conversion.

TIME (S)	CONVERSION (%)		
	40	50	60
20			
40			
60			
80			
100			
120			
140			
160			

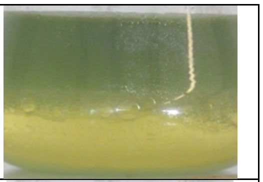
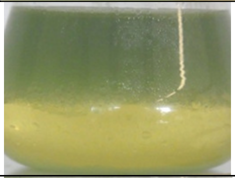
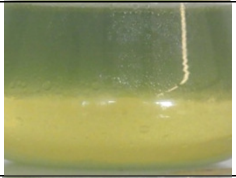
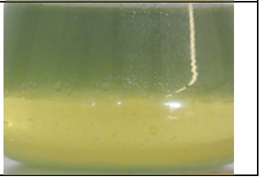
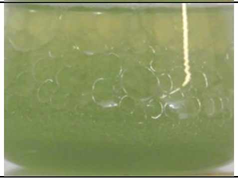
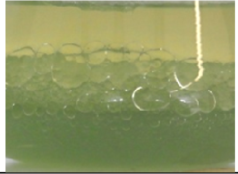
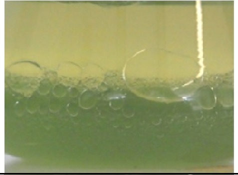
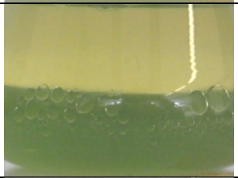
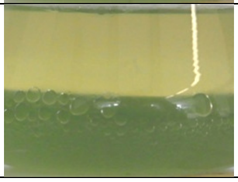
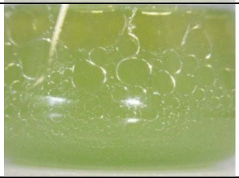
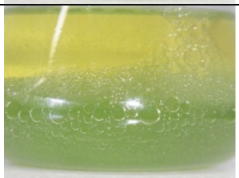
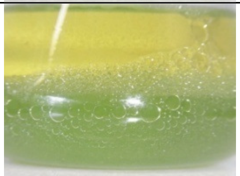
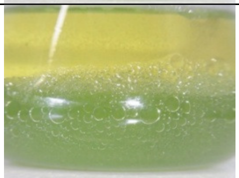
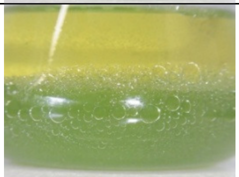
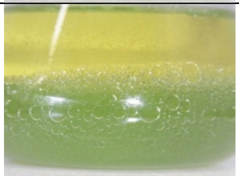
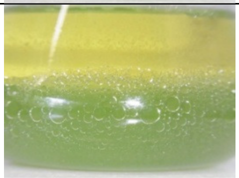
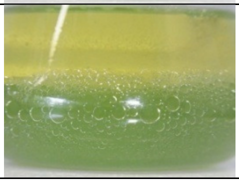
180			
200			
220			
240			

Table 14: The image for settling process every 20 seconds at 70%, 80% and 90% conversion.

TIME (S)	CONVERSION (%)		
	70	80	90
20			
40			
60			
80			
100			
120			
140			
160			

180			
200			
220			
240			
260			
280			
300			
320			
340			

360			
380			
400			
420			
440			
460			
480			
500			

The mixture considered as settled when no droplets formed at the inter phase between the two boundary. At lower conversion, the settling time is fast. This is because, the large amount of methanol and palm cooking oil present in the solution. Due to stability, the settling process will be easier as the palm cooking oil is stable with only small amount of FAME present. K. Gunvachai *et. al.* (2007) highlighted that the present of FAME will be the solubility factor of palm cooking oil into the methanol. But, at the low conversion, small amount of FAME present during this conversion that enable the palm cooking oil to be stable. So, still the settling time is fast and not affected by the present of FAME.

But, as at the higher conversion, more FAME present that means the palm cooking oil is started to destabilize. So, the palm cooking oil will be at the unstable state and dispersed into the methanol phase. Thus the settling time taken for the mixture will be higher because the palm cooking oil molecule is unlikely to settle again each other. But, at 90% conversion, the amount of palm oil in the system is small. So, the FAME rich phase will present at the stable state and thus they are likely to settle and this will lead to a faster settling time.

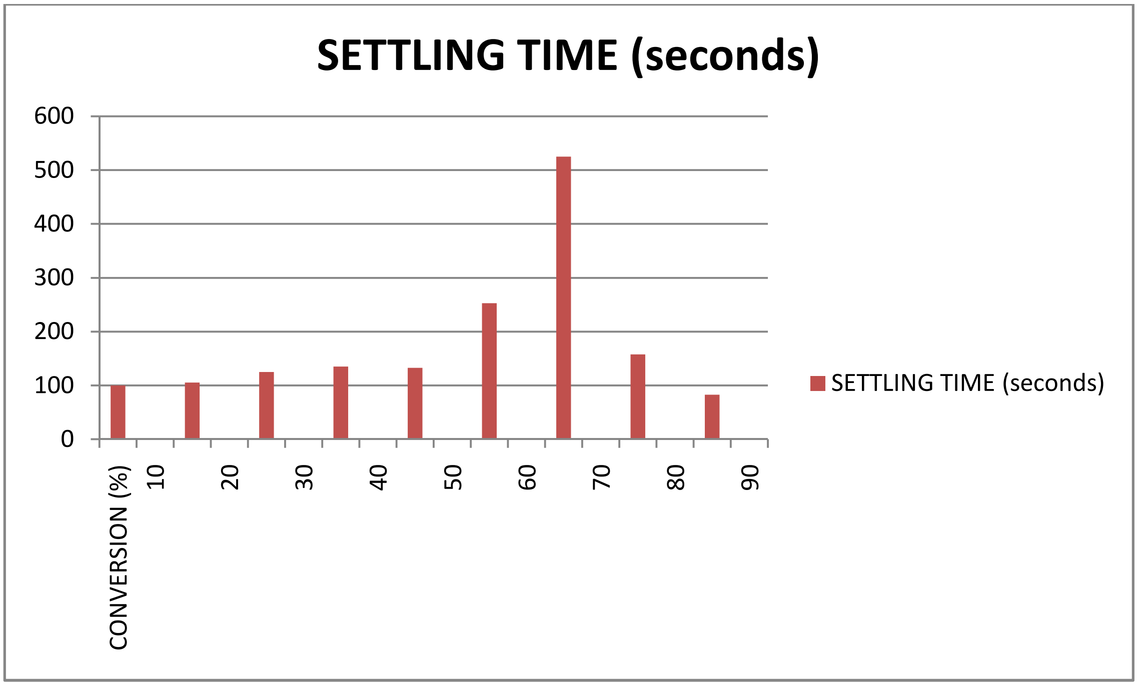


Figure 3. Settling time versus conversion graph.

The intensity of FAME in samples for both upper and lower layer in the mixture at 10% conversion and also at 90% conversion is detected by using the GC analyzer. The FAME compound can be detected from the retention time of 9.5 minutes until 14 minutes. This retention time represent the carbon compound inside the FAME from C16 until C18 (S. Barautian *et, al.,* 2009) The intensity of the FAME inside the sample will represent the amount of FAME inside the sample as compared to the other sample.

Table 15: The intensity of the FAME component inside each sample.

Sample	Intensity of FAME
10% conversion bottom sample	22460
10% conversion top sample	3382
90% conversion bottom sample	8534
90% conversion top sample	273832

Refer appendix for chromatogram.

From the table above, at 10% conversion, the top layer is the layer where the concentration of methanol is high. So, the intensity of FAME inside the top sample is low as compared to the sample at the bottom layer which rich with the palm cooking oil. So, the solubility of FAME is coming into the palm cooking oil as agreement to the previous experiment. While at 90% conversion, the upper layer of the mixture is the region that rich with FAME. AS compared to the bottom layer that rich with the methanol and glycerol, the intensity of FAME will be higher at the upper layer of the mixture. This again agrees with the previous experiment.

While the intensity of FAME is lower at the 10% conversion as compared to the 90% conversion because at higher conversion, more FAME was introduced into the system. At 90% conversion, the mixture will have the methanol and glycerol rich phase together with FAME rich phase while at the lower conversion, the mixture will have only the methanol rich phase and palm cooking oil rich phase. This will explain the reason we have the FAME intensity to be higher at the 90% conversion as compared to 10% conversion for both top and bottom sample.

This experiment also, means to study the solubility of which components actually coming into which component during the reaction. So, the image of the sample in both top and bottom layer at 90% conversion was taken and the comparative picture was taken 1 day later.

Table 16: The Picture of samples right after the separation and 24 hours later.

	Sample picture	
	After separation	**24 hours later**
Top layer (FAME rich phase)		
Bottom layer (methanol and glycerol rich phase)		

After the separation according to their own phase, the samples will be at the cloudy color. In the FAME rich phase, the color will be at cloudy yellow while at the bottom the color had been cloudy green. But, a day after that, both samples turn to their clear solutions. This is because, after the settling process, the solutions still undergo settling process as the micro level. This is because the present of FAME had increase the dispersion of palm cooking oil into the methanol and glycerol rich phase. Also, after one day, at the methanol rich phase, there are some droplets settle at the bottom that should be the FAME and palm cooking oil.

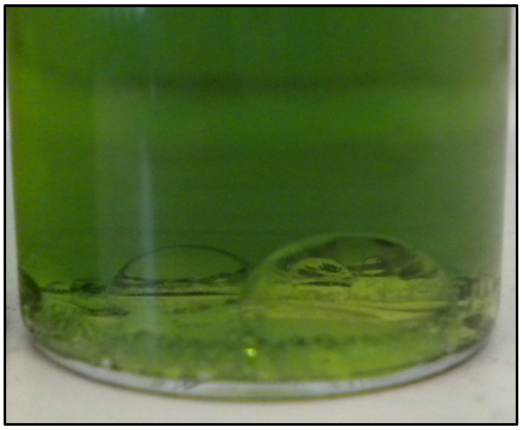


Figure 4: The formation of droplets settle at the bottom of methanol rich phase at 50% conversion

CHAPTER 6

CONCLUSION

From all the experiments, we manage to identify the location for the Transesterification reaction to happen during the biodiesel process. By using the result from the K. Gunvachai *et. al.* (2007) calculation, the result from the experiments able to prove that the reaction actually does happens inside the methanol reach phase in the 2 layer of immiscible liquid. It is more pronounce since the solubility of the catalyst for the reaction is in the methanol part. As the dispersion of palm cooking oil into the methanol increase, the reaction rate will be higher. That the reason why we have a region where the reaction rate is still high even though the palm cooking oil is not miscible in the methanol. The as more palm cooking oil dispersed into the methanol part, the higher the reaction rate as the surface area for the reaction increases (more droplets of palm cooking oil formed).

Also, the formation of FAME had been the driving factor for the palm cooking oil to disperse into the methanol phase. The hydrophilic part of the ester play the role in making the dispersion of palm cooking oil. Even though hindered by the long carbon chain of the ester, the hydrophilic portion of the ester is attracted to the methanol while the long carbon chain of the ester is coming to the palm cooking oil. As the volume of the methanol is large, as to be used in excess, the palm cooking oil is coming into the methanol rich part.

From the result, we can see that at higher conversion (example 70%), the settling process of the system will take a longer time, and this is because the palm cooking oil and FAME solutions present at unstable condition. So, they are unlikely to settle again each other thus the solution will disperse at longer time inside the methanol rich side.

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APPENDICES

To calculate the dispersion of components, we use the correlation factor developed by Selker and Sleicher (1995).

$$\mathrm{X} = \frac{\mathrm{Q_L}}{\mathrm{Q_H}}\left(\frac{\rho_L\mu_L}{\rho_H\mu_H}\right)^{0.3}$$

Q_L=volume of light component
Q_H=volume of heavy component
ρ_L=density of light component
ρ_H=density of heavy component
μ_L=viscosity of light component
μ_H=viscosity of heavy component

For example, the data for the main components as below:

<u>Palm cooking oil</u>	<u>Methanol</u>
Density: 0.907 g/cm^3	Density: 0.792 g/cm^3
Viscosity: 7.52 x 10^{-4} Pa-s (at 25^{o}C)	Viscosity: 5.48 x 10^{-4} Pa-s (at 25^{o}C)
Volume: 35.3 cm^3	Volume: 21.48 cm^3

Substitute into the correlation factor equation give:

$$\mathrm{X} = \frac{21.48}{35.3}\left(\frac{0.792 \text{ x } 5.48 \text{ x } 10^{-4}}{0.907 \text{ x } 7.52 \text{ x } 10^{-4}}\right)^{0.3}$$

$$\mathrm{X} = 0.06$$

Referring into the correlation table below gives the component that dispersed in the reaction.

Correlation Factor, X	Results
<0.3	Light phase always dispersed
0.3-0.5	Light phase probably dispersed
0.5-2.0	Phase inversion possible
2.0-3.3	Heavy phase probably dispersed
>3.3	Heavy phase always dispersed

To calculate the amount of each components present during the reaction as specified conversion level. We use the amount of the palm cooking oil as the basis. Let say, the initial amount of palm cooking oil at 0% conversion is 30g. Molecular weight of the palm cooking oil is 271.7 g/mol

The number of mol of the palm cooling oil used initially = $\frac{30\ \mathrm{g}}{271.79\ \mathrm{g/mol}}$

= 0.11 mol

Based on the stoichiometry ratio between methanol and palm cooking oil is 3:1, the number of mol of methanol required for the reaction is 3 x 0.11 mol = 0.33 mol

With respect to the literature study, the amount of methanol used in the reaction is 300 mol% excess, the total amount of methanol used is 3 x 0.33 mol = 0.99 mol.

The molecular weight of methanol is 32.034 g/mol. So, the mass of methanol used in the reaction is 0.99 mol x 32.034 g/mol = 31.7 g.

The mass of FAME and glycerol initially is 0 g because the reaction is not yet happen.

To calculate at other conversion level, we use the 0% conversion level as the basis. For example at 50% conversion.

The amounts of the components present at this conversion are:

- Palm cooking oil

  $\frac{50}{100}$ x 0.11 = 0.055 mol

  The mass of palm cooking oil used = 0.055 mol x 271.79 g/mol

  = 14.95 g

- Methanol

$\frac{50}{100}$ x 0.33 = 0.165 mol + 0.66 mol = 0.825 mol

The mass of methanol used = 0.825 mol x 32.034 g/mol

= 26.43 g

- Glycerol

Glycerol is produced throughout the reaction. So, the formation of the glycerol is equal to the number of mol of palm cooking oil consumed in the reaction.

At 50% conversion, the number of mol of glycerol is 0.055 mol. Thus, the mass of the glycerol is 0.055 mol x 92.09 g/mol = 5.065 g.

- Fatty acid methyl ester (FAME).

The formation of fame is as according to the reaction conversion. At 50% conversion, the amount of FAME produced can be calculated by using the mass balance. The total amount of the reactant, methanol at 0 mol% excess plus with palm cooking oil minus the amount of byproduct, glycerol will give the amount the FAME that used at 50% conversion.

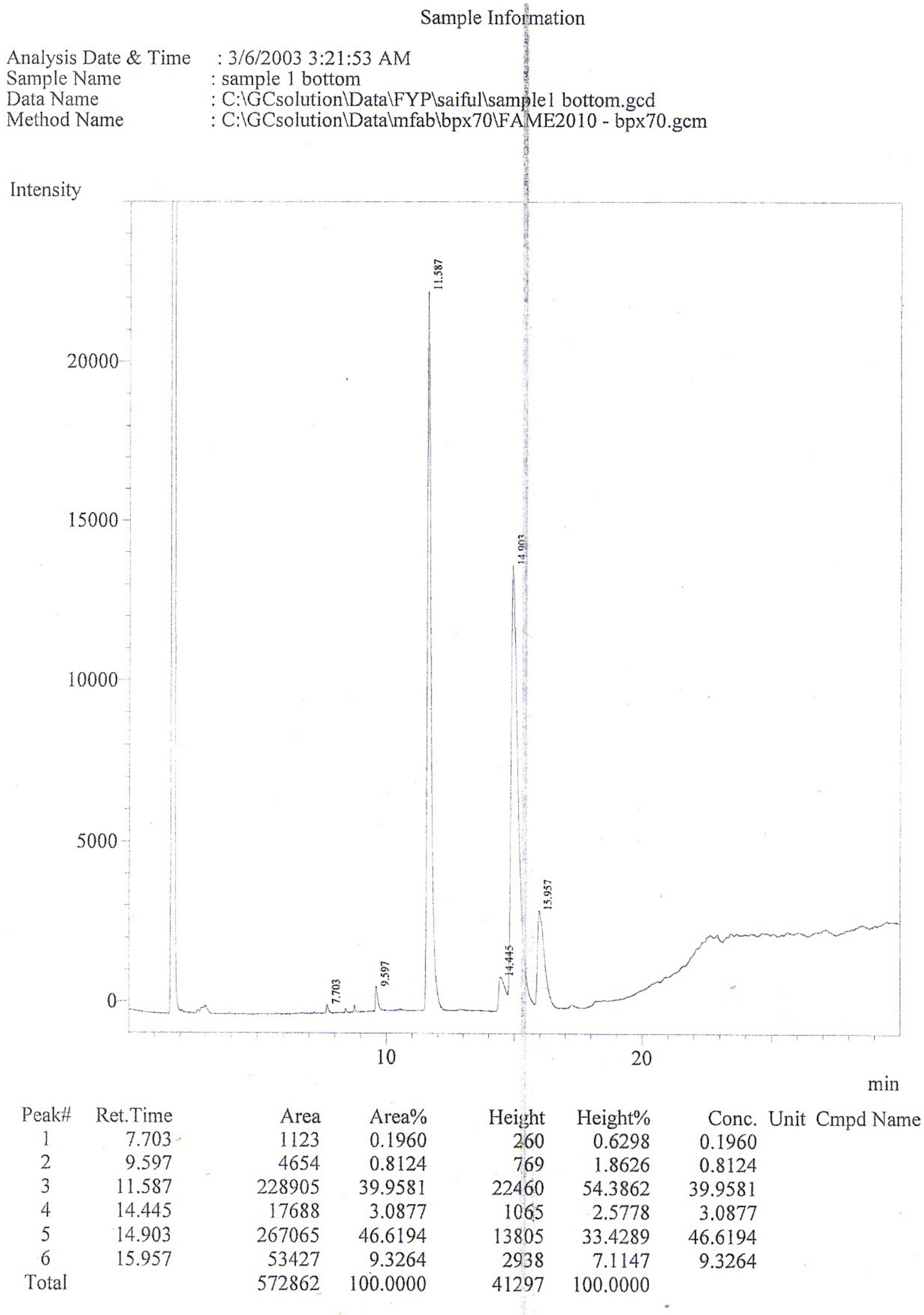
Amount of methanol at 0% excess = 0.165 mol x 32.04 g/mol

= 5.29 g

Total amount reactant: 14.95 g + 5.29 g = 20.24 g

Total amount of FAME present: 20.24 g – 5.065 g = 15.18 g

Chromatogram for 10% conversion bottom sample

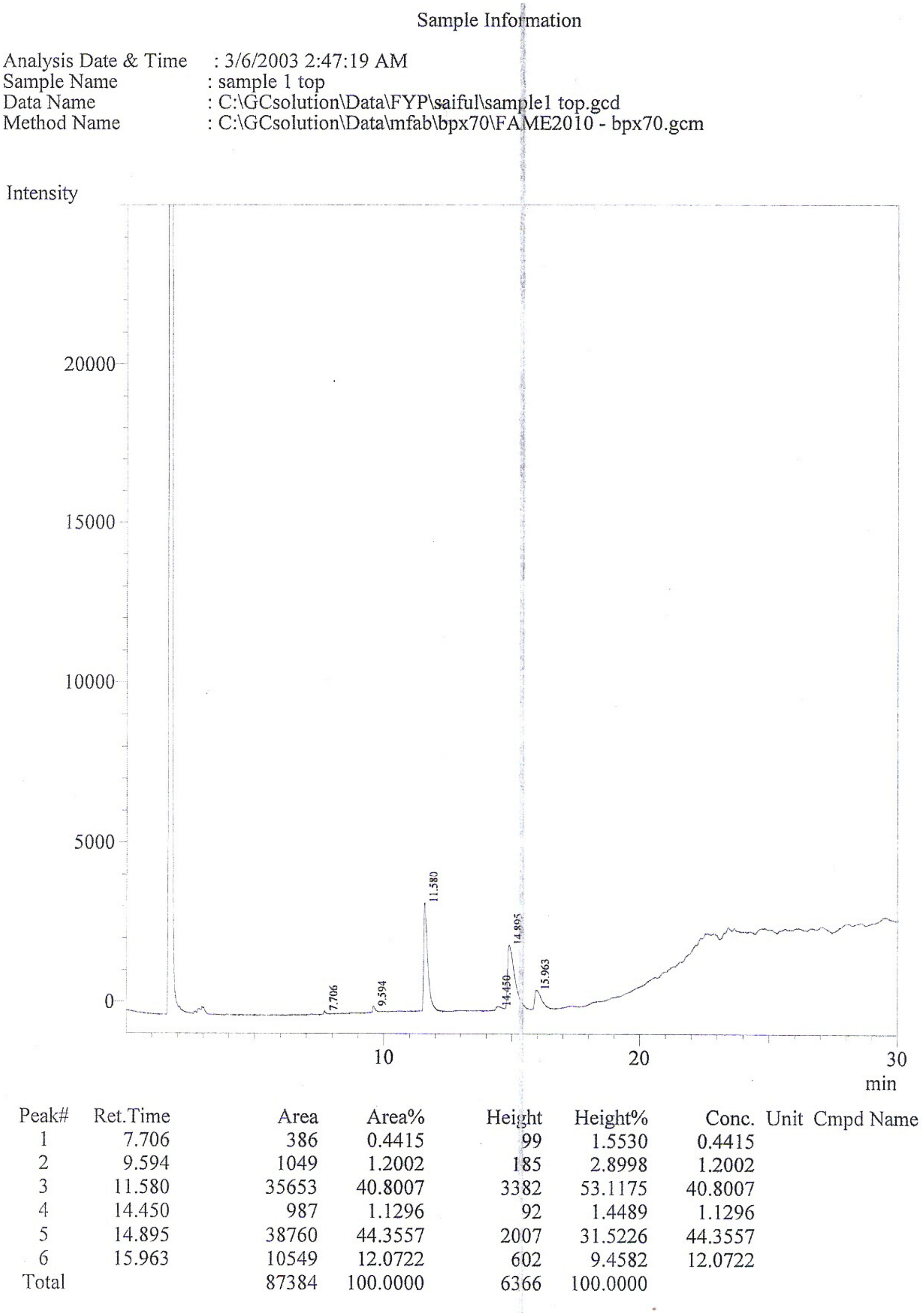


Sample Information

Analysis Date & Time : 3/6/2003 3:21:53 AM
Sample Name : sample 1 bottom
Data Name : C:\GCsolution\Data\FYP\saiful\sample1 bottom.gcd
Method Name : C:\GCsolution\Data\mfab\bpx70\FAME2010 - bpx70.gcm

Peak#	Ret.Time	Area	Area%	Height	Height%	Conc.	Unit	Cmpd Name
1	7.703	1123	0.1960	260	0.6298	0.1960		
2	9.597	4654	0.8124	769	1.8626	0.8124		
3	11.587	228905	39.9581	22460	54.3862	39.9581		
4	14.445	17688	3.0877	1065	2.5778	3.0877		
5	14.903	267065	46.6194	13805	33.4289	46.6194		
6	15.957	53427	9.3264	2938	7.1147	9.3264		
Total		572862	100.0000	41297	100.0000			

Chromatogram for 10% conversion top sample

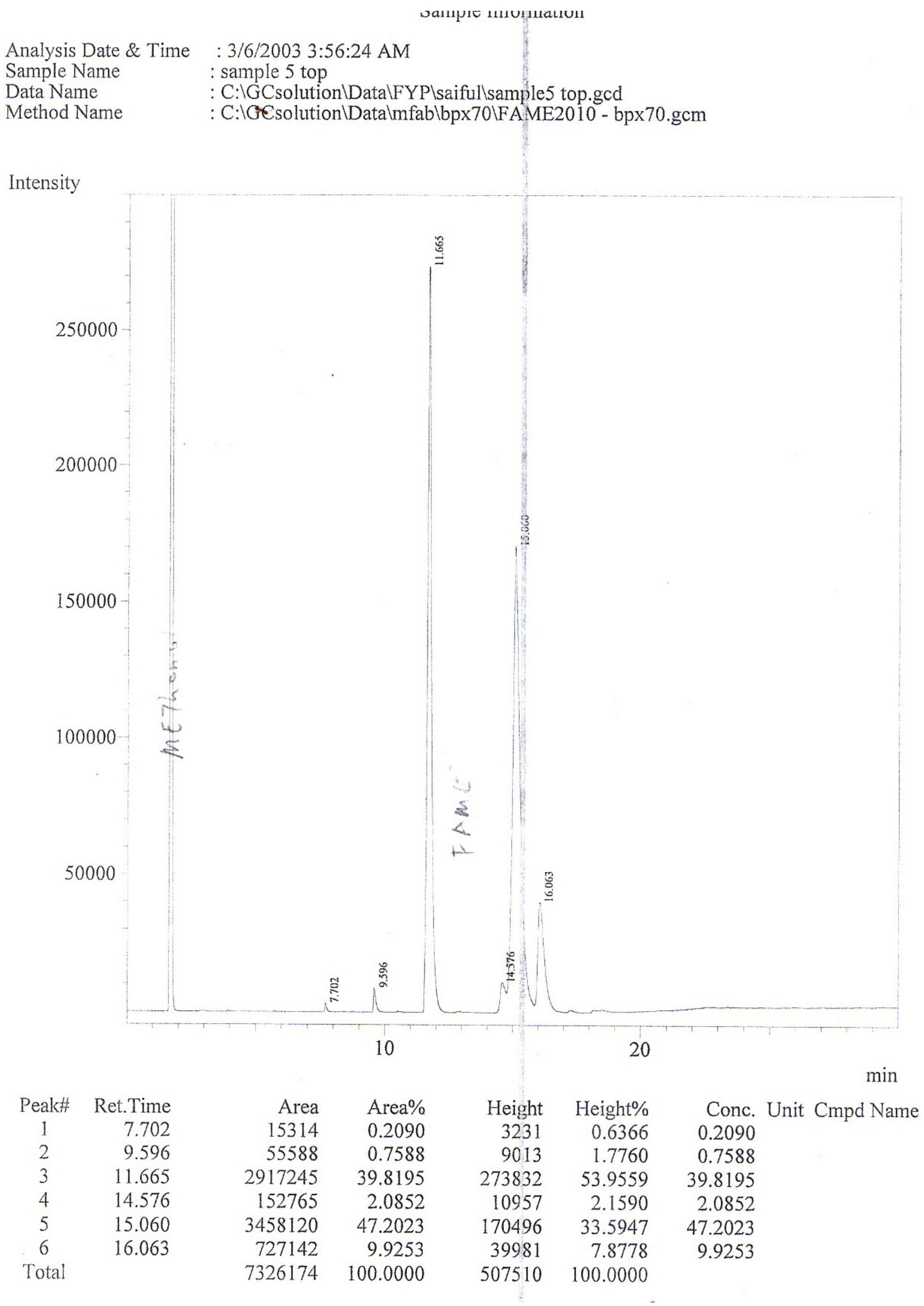


Sample Information

Analysis Date & Time	: 3/6/2003 2:47:19 AM
Sample Name	: sample 1 top
Data Name	: C:\GCsolution\Data\FYP\saiful\sample1 top.gcd
Method Name	: C:\GCsolution\Data\mfab\bpx70\FAME2010 - bpx70.gcm

Peak#	Ret.Time	Area	Area%	Height	Height%	Conc.	Unit	Cmpd Name
1	7.706	386	0.4415	99	1.5530	0.4415		
2	9.594	1049	1.2002	185	2.8998	1.2002		
3	11.580	35653	40.8007	3382	53.1175	40.8007		
4	14.450	987	1.1296	92	1.4489	1.1296		
5	14.895	38760	44.3557	2007	31.5226	44.3557		
6	15.963	10549	12.0722	602	9.4582	12.0722		
Total		87384	100.0000	6366	100.0000			

Chromatogram for 90% conversion top sample



Sample Information

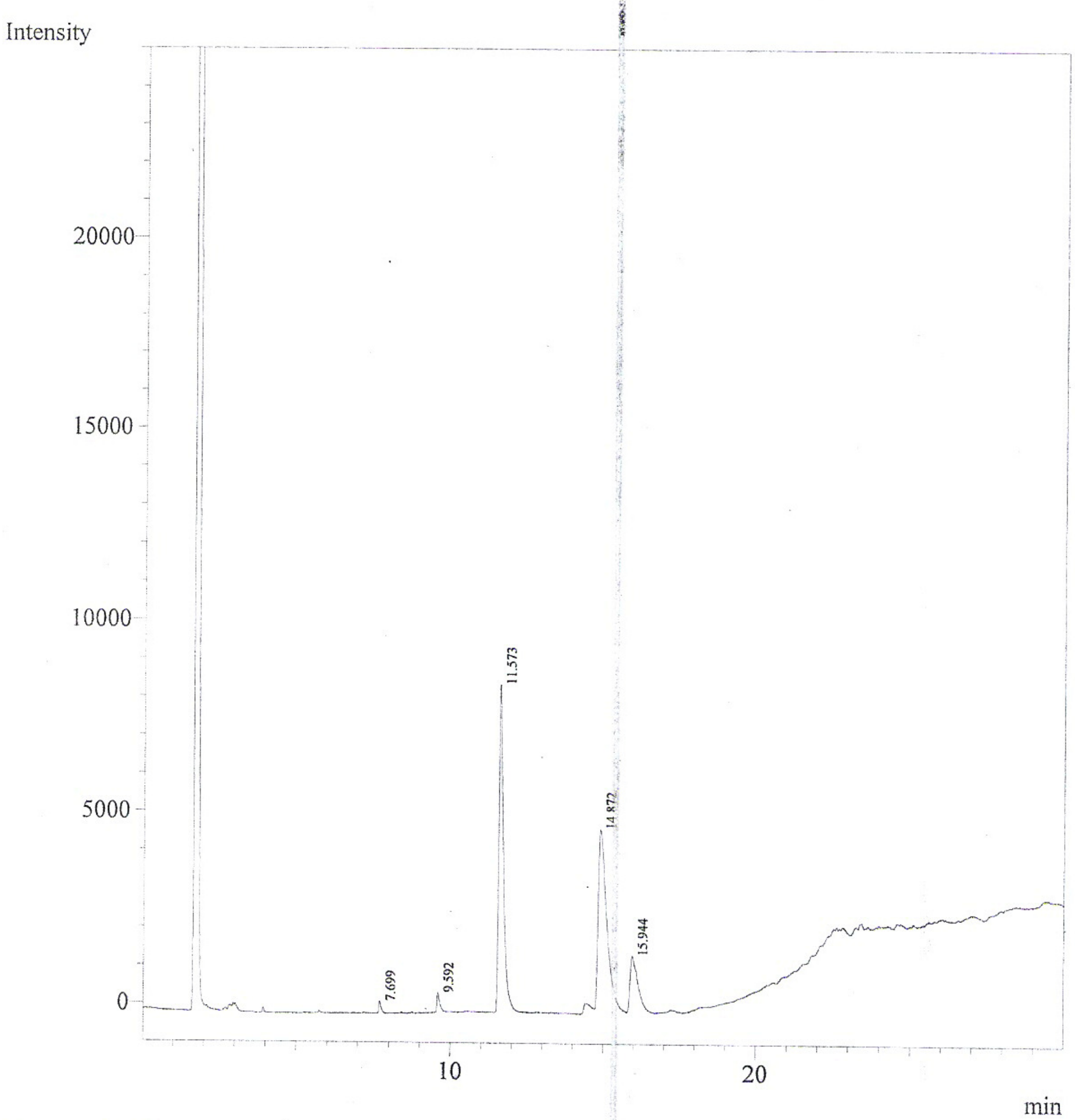
Analysis Date & Time : 3/6/2003 3:56:24 AM
Sample Name : sample 5 top
Data Name : C:\GCsolution\Data\FYP\saiful\sample5 top.gcd
Method Name : C:\GCsolution\Data\mfab\bpx70\FAME2010 - bpx70.gcm

Peak#	Ret.Time	Area	Area%	Height	Height%	Conc.	Unit	Cmpd Name
1	7.702	15314	0.2090	3231	0.6366	0.2090		
2	9.596	55588	0.7588	9013	1.7760	0.7588		
3	11.665	2917245	39.8195	273832	53.9559	39.8195		
4	14.576	152765	2.0852	10957	2.1590	2.0852		
5	15.060	3458120	47.2023	170496	33.5947	47.2023		
6	16.063	727142	9.9253	39981	7.8778	9.9253		
Total		7326174	100.0000	507510	100.0000			

Chromatogram for 90% conversion bottom sample

Sample Information

Analysis Date & Time : 3/6/2003 4:31:02 AM
Sample Name : sample 5 bottom
Data Name : C:\GCsolution\Data\FYP\saiful\samle5 bottom.gcd
Method Name : C:\GCsolution\Data\mfab\bpx70\FAME2010 - bpx70.gcm



Peak#	Ret.Time	Area	Area%	Height	Height%	Conc.	Unit	Cmpd Name
1	7.699	1456	0.7079	311	2.0070	0.7079		
2	9.592	3016	1.4663	508	3.2827	1.4663		
3	11.573	87358	42.4759	8534	55.1204	42.4759		
4	14.872	88519	43.0405	4673	30.1805	43.0405		
5	15.944	25316	12.3094	1457	9.4093	12.3094		
Total		205666	100.0000	15482	100.0000			