Production of Fatty Acid Methyl Esters (FAME) from Ceiba Pentandra Using Microwave Assisted Technique and Benzyltrimethyl Ammonium as Catalyst

by

Rhamadril Rafiq Johari

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(AP Dr Suzana Yusup)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

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 excepts 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.

RHAMADRIL RAFIQ JOHARI

ABSTRACT

Being known as one of the most important source of energy, fossil fuel is definitely the most desirable one due to its great advantages and potentials. Unfortunately, as time goes by, people around the globe are aware of the fact that the total amount of the fossil fuel is depleting each day up to 2013. Nevertheless, the circumstances somehow act like a 'wake up call' for another renewable and sustainable source of energy, which is named as Biodiesel. This is one of the latest technologies that is currently undergoing massive researches since it is the most suitable to replace the fossil fuel in the future for the sack of the next generation. The idea of producing Biodiesel by using 2-step transesterification and conventional solvent, methanol and catalyst Potassium Hydroxide (KOH) and sulfuric acid, H2SO4 respectively has been well established worldwide. Hence, this project is about to make huge modification; in which Ceiba Pentandra (Kapok seed oil) is still chosen as the raw material and methanol as the solvent whereas the catalyst will be replaced by an amine based catalyst, Benzyltrimethyl Ammonium. Hence, the main purpose of the project is to discover the optimum parameters such as the methanol to oil ratio, catalyst concentration, microwave irradiation time and temperature only by applying 1-step transesterification process only with the assistance of energy stimulant microwave technique. Based from the results, the highest FAME yield (89.81%) is obtained at the methanol to oil ratio is 14:1, 3% catalyst concentration, 70 degree Celcius for 2 minutes irradiation time. Furthermore, the application of microwave technique has successfully reduced the reaction time as well as the total energy consumption for the transesterification process. Lastly, the properties of the FAME produced under the optimum parameters are characterized by using the international standard of Biodiesel (ASTM 6751 & EN 14214).

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CHAPTER 1

INTRODUCTION

1.1 Background

2013, the era in which oil acquisition and consumption is dominating the course of national and international politics throughout the globe, thoroughly. The truth is our dependence on oil is responsible for many of the greatest environmental, health, and security problems faced by the nation nowadays as quoted from the Diesel Fuel Tech Review (2007). Therefore, searching for a light to ease our dependence on oil will certainly present one of the biggest challenges of all. In 2010, diesel fuel accounted for 4625 kt of oil equivalent of total vehicle fuel consumption in Malaysia which is so much higher from the consumption in 1971, that is 630 kt of oil equivalent. The introduction of a new technology known as Biodiesel is one of the most practical and effective solution to overcome this crucial issue. Knothe (2007) defined it as the mono alkyl ester of long chain fatty acid derived from the vegetable oil and animal fat. Air Quality UK (2011) states that its main advantages are relatively clean-burning, renewable fuel produced from new and used animal and vegetable oil and others. Moreover, Biodiesel has three large potentials over regular petroleum diesel. First, it is not a petroleum-based fuel and this indicated that it would reduce our dependency on foreign oil. Next, biodiesel is produced domestically and by doing so, it creates job opportunities and contributes to local economies nationwide. Last but not least, Biodiesel is much cleaner than conventional diesel since it produces less harmful emissions than regular petroleum diesel, especially when it is burned in a combustion engine. Nevertheless, direct utilization of vegetable oil is not recommended due to viscosity problem (Ramadhas et al., 2003). As far as the author concern, up to this extent there is no reported literature emphasizing on utilization of Ceiba Pentandra seed oil by using microwave technique for biodiesel production as well as choosing Benzyltrimethyl Ammonium as the catalyst. Therefore, this project attempts to explore the potential of utilizing Ceiba Pentandra seed oil as the biodiesel feedstock by using microwave technology and the particular catalyst mentioned previously.

Based from the Olduvai theory, the life expectancy of Industrial Civilization is approximately 100 years; the range of 1930 to 2030. Institute on Energy and Man (2001) has found that during the period there will be a fall of the Industrial Civilization due to the depreciation of fossil fuel. The worst impact is the human civilization will be facing the fate of collapse. Nevertheless, it is found that the global population is expected to increase by approximately 3 billion people by 2050. Apparently the extreme increment will certainly create a major problem as well as affecting the population, industry, transportation and eventually the cost of fossil fuels will grow dramatically. Therefore, the highly potential and latest technologies are needed for fuel extraction by using feedstocks, which will not threaten food security, cause minimal or even no loss of natural habitat and soil carbon.

Furthermore, waste management has to be improved and environmental pollution should be minimized or eliminated. Fortunately, Biodiesel from plant biomass are sustainable and provide clean energy for the coming generations. In fact, the technology is expected to foster recycling of agricultural feedstocks and also improve soil fertility and human health.

1.2 Problem Statement

i. What are the optimized conditions for the production of Ceiba Pentandra biodiesel using microwave assisted technique, with the presence of Benzyltrimethyl Ammonium as the catalyst?

ii. Will microwave assisted technology and Benzyltrimethyl Ammonium enhance the oil and fatty acid alkyl ester yield derived from Ceiba Pentandra seed?

iii. Will energy consumption be reduced with the application of microwave assisted transesterification as opposed to conventional transesterification process?

iv. How significant is the difference of composition, yield and conversion of FAME if compared with the research done previously using conventional catalyst (KOH) and 2-step process.

1.3 Objectives

i. To investigate the optimum operating condition for the microwave assisted transesterification of Ceiba Pentandra seed oil including the effects of solvent to oil ratio, catalyst concentration, microwave irradiation time and temperature by using Benzyltrimethyl Ammonium as the catalyst.

ii. To characterize the oil and the biodiesel product following international standard (ASTM 6751 & EN 14214).

1.4 Scope of Study

For this project the scope of study will be only on the lab scale since many experiments will be conducted in order to investigate the associated parameters such as the solvent to oil ratio, concentrations of catalyst, time and temperature and the effects on the esterification and transesterification process accordingly. Furthermore, this project will also focus on the significance of using the microwave techniques since the previous studies show that it has produced positive outcomes in terms of the reaction rates as well as the alternative routes, if relatively compared with the conventional heating. The response surface methodology (RSM) which is a collection of mathematical and statistical techniques for empirical model building will be used for the optimization purpose. Moreover, comparison will be made between results of experiments by using both types of heating, with the presence of Benzyltrimethyl Ammonium as the catalyst. Plus, study will also be made to see if microwave heating is able to reduce the overall energy consumption for biodiesel production. Lastly, the biodiesel produced from optimized condition with highest yield is to be characterized and compared with the international standard of biodiesel. The European biodiesel standard, EN 14214 and American standard, ASTM 6751 are used as reference. The properties of biodiesel to be characterized are:

- ☐ Density
- ☐ Acid value
- ☐ Water content
- ☐ Flash point
- ☐ Cloud point
- ☐ Pour point
- ☐ Oxidative stability
- ☐ Kinematic viscosity
- ☐ Cetane number
- ☐ Higher heating value
- ☐ Sulphur content
- ☐ Cold filter plugging point

CHAPTER 2

LITERATURE REVIEW

2.1 Ceiba Pentandra and Benzyltrimethyl Ammonium

Kapok tree or its scientific name ''Ceiba Pentandra' is one of the most gigantic trees found in the jungle. The main reason is merely because it can reach up to 200 feet in height, in fact, it can possible grow as much as 13 feet per year. Moreover, the trunk can expand up to 10 feet in diameter and basically it acts as the shelter to the variety of species including frogs, birds and others. One of the typical properties of this tree is the seeds will be blown into open areas, which means it could be the first to colonize open areas in the forest. Nevertheless, the kapok tree spread its seeds at its best, in which there will be producing anywhere between 500 and 4,000 fruits at once, and each fruit containing up to 200 seeds. Then these fruit burst open, silky fibers spread the many seeds all over the forest. In most cases, it is found throughout the Neotropics, from southern Mexico to the southern Amazon and even some parts in West Africa. In terms of the advantages, Kapok tree is also useful to the daily life since it used as an alternative to down as filling in mattresses, pillows and others but in this project the main part of this tree to be investigated is its seed oil, which is highly potential in the production of Biodiesel. Plus, the unconventional catalyst used in this project is known to be Benzyltrimethyl Ammonium. It is strongly believed that this particular catalyst will give significant effects on the production of the Fatty acid methyl esters when associated with appropriate solvents under certain temperature and pressure. Certain physiochemical properties of Ceiba Pentandra seed oil have been analyzed by Salimon and Khairul Asmak (2005) and it is shown in *Table 2.1.*

Table 1: Physiochemical properties of Ceiba Pentandra seed oil

Properties	Average value
Water content (%)	0.04
Refractive index (at 28℃)	1.46
Free Fatty Acid, FFA (%)	15.3

Saponification value (mg/g)	208
Iodine value	104

The fatty acid composition of Ceiba Pentandra seed oil shown in *Table 2.2* was presented in different research work.

Table 2 : Fatty acid composition of Ceiba Pentandra

Ceiba Pentandra seed oil	Fatty Acid Composition (wt%)		
	Berry, K. (1979)	Enser, M. (1991)	Yusup et al.
Caproic acid (C16)	-	-	9.42
Myristic acid (C14)	0.25	-	-
Palmitic acid (C16)	24.31	20.90	23.17
Palmitoleic acid (C16:1)	0.40	-	-
Stearic acid (C18)	2.65	13.70	4.73
Oleic acid (C18:1)	21.88	20.80	22.88
Linoleic acid (C18:2)	38.92	42.60	30.00
Linolenic acid (C18:3)	1.00	1.9	-
Arachidic acid (C20)	-	-	1.18

From the table above, it shows that the value of fatty acid was determined in weight percentage and it can be directly seen that Ceiba Pentandra seed oil contained high linoleic acid (unsaturated fatty acid). In fact, any oil containing unsaturated fatty acid is probably an excellent oil for engine performance during cold weather after conversion to biodiesel (Yusup and Khan, 2010).

Please take note that the determination of free fatty acid (FFA) content in the oil is crucial before proceeding to transesterification process. For instance, feedstock containing less than 2 to 3% of FFA content, required no pre-treatment process and one-step direct transesterification reaction is sufficient enough to produce high quality biodiesel (Thamsiriroj and Murphy, 2010). Higher content of FFA will reduce the overall conversion of FFA to FAME through base catalyzed transesterification. Consequesntly, two-step acid catalyzed esterification and base-catalyzed transesterification process have been introduced to reduce the FFA content in seed oil to less than 1% and maximize the conversion of FFA to FAME (Ye et al., 2010).

2.2 Esterification and Transesterification

Basically esters are derived from carboxylic acids. However, esterification is relatively slow although it can give higher biodiesel yield compared to transesterification reaction and it requires the reactor to be in acidic environment (Dube et al., 2007). Naturally a carboxylic acid contains the -COOH group, and in an ester the hydrogen in this group is replaced by a hydrocarbon group. In most cases the hydrocarbon group is alkyl, but it is also possible to have aryl groups. Esterification takes place when carboxylic acids are heated with alcohols in the presence of a catalyst (acid or alkali) and it is usually concentrated sulphuric acid. Moreover, take note that it is both slow and reversible reaction. The equation for the reaction between an acid RCOOH and an alcohol R'OH (where R and R' can be the same or different) is:

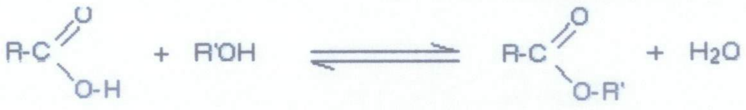


Figure 1: The esterification process

For instance, to produce ethyl ethanoate from ethanoic acid and ethanol, the equation would be:

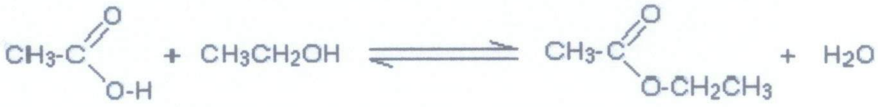


Figure 2: The example of an esterification proces

These soap and emulsion formations make separation of product and by-product of biodiesel become longer and harder (Serioet et al., 2008). Therefore, acid catalyzed esterification reaction is essestial to reduce the FFA content in the seed oil below 1% to avoid shortcoming of the subsequent reaction, which is based-catalyzed transesterification (Gerpen, 2005).

Next term is known as transesterification process, which means a reversible reaction in which one ester is converted into another (as by interchange of ester groups with an alcohol in the presence of a base). Also known as alcoholysis, transesterification is the well-established chemical reaction of vegetable oils and animal fats with an alcohol to from fatty acid alkyl esters and glycerol (Leung et al., 2010). Yan et al. (2009) states that the main objective of transesterification is to overcome problems due to the fact that vegetable oils and animal fats cannot be used directly in diesel engines because of the nature of its high viscosity and low volatility. Since the reaction is reversible, excess alcohol is practically used to shift the equilibrium to the product side and thus raising the product yield (Srivastava and Prasad, 2000).

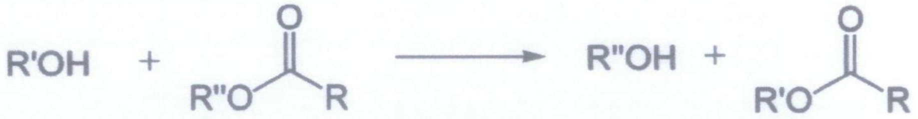


Figure 3: The transesterification process

In short, it merely mean the addition of alcohol to the ester to produce different alcohol as well as different ester. This process has few applications in daily life such as the Polyester production, Methanolysis and biodiesel production and others.

2.3 Effects of Solvent and Catalyst

It is good to acknowledged that most of the biodiesel nowadays is produced from the refined or edible type oils by using the conventional catalyst and solvent, methanol and an alkaline catalyst respectively. Although it is presumed that there will be no problems regarding the sources of the raw materials, one of the main drawbacks of the alkaline-esterification of these oils is that they normally contain large amounts of free fatty acids (FFA). What happen is that these FFAs will promptly react with the alkaline catalyst to produce soaps, which will then prevent the separation of ester and glycerin. Therefore, a two-step transesterification process is introduced in order to convert the high FFA oils to its mono-esters. In short, there are two main mechanisms involved for this process to occur successfully. HJ Berchmans (2008) states that acid catalyzed esterification reduces the FFA content of the oil to less than 2% whereas during the second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and also glycerol. Bear in mind that the major factors affecting the conversion efficiency of the process are the molar ratio, amount of catalyst, reaction temperature as well as the reaction duration. Eventually, this project is expected to support the production of biodiesel from the Kapok seed oil as a viable alternative to the diesel fuel by using the Benzyltrimethyl Ammonium as the high potential catalyst.

2.4 Microwave Technique

As discussed previously, most high potential raw material sources to produce biodiesel oils are characterized by their high free fatty acid contents. Up to this extent, the conventional transesterification technique for the production of biodiesel has already been well established. Plus it is is the best and easiest step in producing a cleaner and environmental friendly fuel (Meher et al., 2006). Therefore, for this project, the study is very much interested to investigate an alternative energy stimulant, known as the 'microwave irradiation', to produce of the sustainable energy source, biodiesel. Since the optimum parametric conditions from the conventional technique have been obtained in the previous studies, hence this technique will be utilized for the purpose of comparing the two different systems. The good news is that previous study showed that the application of radio frequency microwave energy eventually provide a fast and easy route with several advantages such as enhancing the reaction rate and also improving the separation process. From the research done, Reefat et al. (2008) obtained the optimum parametric conditions for biodiesel production by using used cooking oil and the conventional heating technique and it was compared with the microwave irradiation method. Under the same optimal reaction conditions, microwave irradiation was able to make the production of biodiesel very fast (2 minutes) compared with the conventional technique (60 minutes) and also increased the yield to 100%. Lertsathapornsuk et al. (2003)

reported that the microwave irradiation has successfully decreased the reaction time in 10 seconds to complete the transesterification process from used cooking oil. Also, Kumar et al. (2011) investigated the microwave assisted alkali catalyzed transesterification of Pongamia pinnata seed oil. It was found that the biodiesel was succesfully produced by microwave assisted reaction within 5-10 minutes compared to conventional heating which required about 3 hours for the reaction. Overall, researches had proven that microwave assisted technique enhance the production of biodiesel in terms of reaction time and yield. Thus, the project will concentrate on exploratory of utilizing microwave technology with Ceiba Pentandra as the feedstock for biodiesel production and the presence of Benzyltrimethyl Ammonium as the catalyst.

CHAPTER 3

METHODOLOGY

3.1 PROJECT FLOW CHART

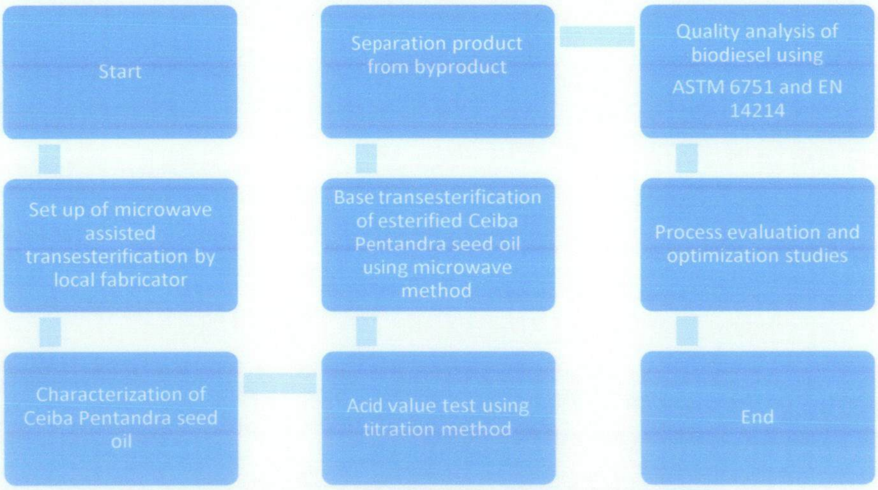


Figure 4: Flow chart of research activities

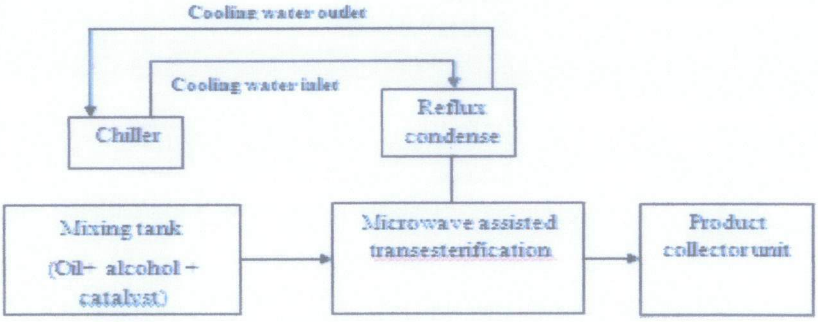


Figure 5: Block diagram of the proposed experimental process

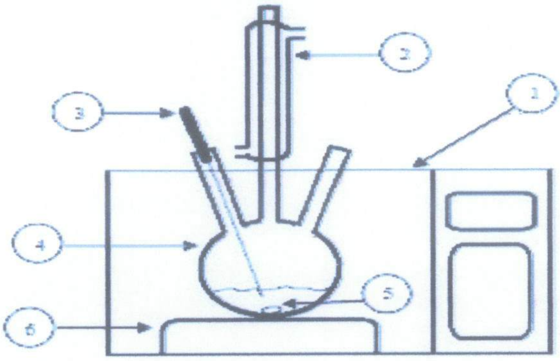


Figure 6: Schematic diagram of microwave system for batch experiments 1. Microwave oven, 2. Condenser, 3. Thermocouple, 4. Three-neck round bottom flask, 5. Magnetic bar, 6. Base

3.1.1 Acidity Test

Acidity test is done to check the free fatty acid content (FFA) in the crude kapok seed oil as well as the esterified seed oil. The manual titration is an adaptation of AOCS Method Cd 3d-63.

Reagents:

Titrant : KOH (85% Assay); 0.66g KOH/500mL Isopropanol = 0.02M Solvent Isopropanol:Toluene ratio (1:1)

Indicator : 1.0 g Phenolphtalein/100mL Isopropanol = 1%

Procedure:

1. KOH titrant is filled into a burette and the initial volume is noted.
2. 25mL of solvent is poured into a conical flask with 2 – 3 drops of indicator.
3. Titrant is added into the solvent drop-wise with regular stirring until faint pink colour remains.
4. The amount of titrant used is recorded.
5. 2 g of sample (exact weight is noted) is added into the flask and mixed well.
6. KOH titrant is again added drop-wise with regular stirring until faint pink colour remains.

7. The volume of titrant used is recorded.

The equation below is used to determine the acid value of kapok seed oil:

$$Acid\ value = \frac{(A - B) \times M \times MW_{KOH}}{W}$$

Where, A = Volume of titrant used for sample

B = Volume of titrant used for blank

M = Molarity of titrant

MW = Molecular weight for KOH W = Exact weight of sample

3.1.2 Esterification

Esterification which uses acid as catalyst is aimed to reduce the free fatty acid (FFA) content in the oil to less than 1%. It is vital to prevent the occurrence of saponification in transesterification later on. Hence, separation of biodiesel from by-products will be easier and it also increases the yield of biodiesel. The operating conditions of acid esterification are at 65°C, 10:1 molar ratio of methanol to oil, 1 wt% catalyst and 5 minutes reaction time.

Procedure:

1. 250g of kapok seed oil is weighed.
2. Measuring cylinder is used to measure methanol of 10:1 molar ratio to oil.
3. 1.0 wt% of sulphuric acid is added to mix with the sample and methanol.
4. The mixture is then poured into the three-neck round bottom flask and heated to 65 °C in the microwave system.
5. When the temperature reaches 65 °C, the heating is continued for 5 minutes.
6. Upon completion of reaction, the content is poured into a separating funnel and left to settle into two layers for 24 hours.
7. The lower layer of by product is removed.

8. Warm de-ionized water is used to wash the esterified oil for several times until the pH value of washing water close to 7.0.

3.1.3 Transesterification

Transesterification process converts long chain of fatty acid in the seed oil to mono-ester. The process reduces the viscosity of the oil and fats, so that it can be used as proper alternative for diesel fuel. The experiments are designed using the response surface methodology (RSM) to investigate the optimized conditions for production of Ceiba Pentandra biodiesel using microwave assisted technique. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response. It is able to explore the relationships between several explanatory variables and one or more response variables. *Table 3.1* shows the designed experiments which consist of 30 runs where the variables being studied are methanol-to-oil ratio, amount of catalyst, reaction temperature and reaction time.

Table 3.1: Designed experiments for transesterification

Run	**Methanol:Oil**	**Catalyst amount (wt%)**	**Temperature** (degree Celcius)	**Time** (min)
1	10.00	2.00	55.00	0.50
2	10.00	4.00	55.00	3.50
3	10.00	2.00	55.00	3.50
4	14.00	3.00	70.00	2.00
5	10.00	2.00	55.00	3.50
6	14.00	1.00	40.00	5.00
7	6.00	1.00	70.00	2.00
8	6.00	3.00	70.00	5.00

Procedure:

1. 50g of kapok seed oil is weighed.
2. Measuring cylinder is used to measure the ratio of methanol required.
3. Benzyltrimethyl Ammonium is added and mixed with the sample and methanol.
4. The mixture is poured into the three-neck round bottom flask and heated to the desired temperature in the microwave system.
5. The reaction is started once the desired temperature is reached.
6. Upon completion of reaction, the content is poured into a separating funnel and left to settle into two layers for 24 hours.
7. The lower layer of by product is removed.
8. Warm de-ionized water is used to wash the esterified oil for several times until the pH value of washing water close to 7.0.
9. Rotary evaporator is used to remove excess moisture and methanol from the biodiesel.
10. 20 wt% of sodium thiosulphate is used to remove moisture from the oil.
11. The sodium thiosulphate is filtered off from the oil after around 1 hour.

3.1.4 Characterization of Biodiesel

The biodiesel produced from each run of experiment will be analyzed for the percentage of fatty acid methyl ester (FAME) using the gas chromatography. Upon obtaining the response of each run, the results are used in RSM to obtain the optimized conditions for highest yield of biodiesel production. The quality attributes and fuel properties of the biodiesel produced under the optimum conditions will be evaluated by determining its physical and chemical parameters. The properties to be tested include density, acid value, water content, flash point, cloud point, pour point, oxidative stability, kinematic viscosity, cetane number, higher heating value, sulphur content, and cold filter plugging point following recommended American Standards for Testing and Materials (ASTM 6571) and European Standard (EN14124).

3.2 Key Milestone

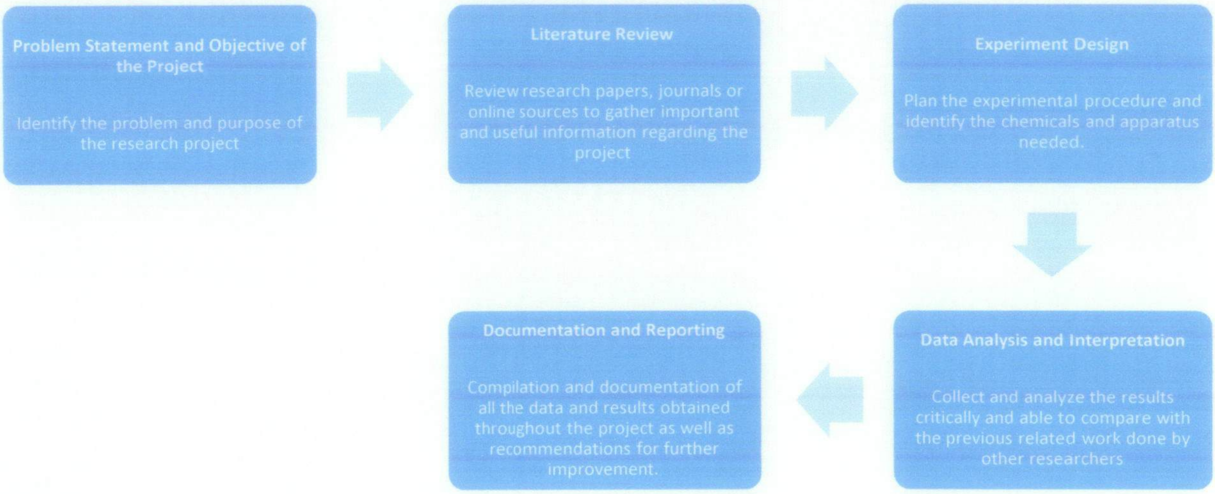
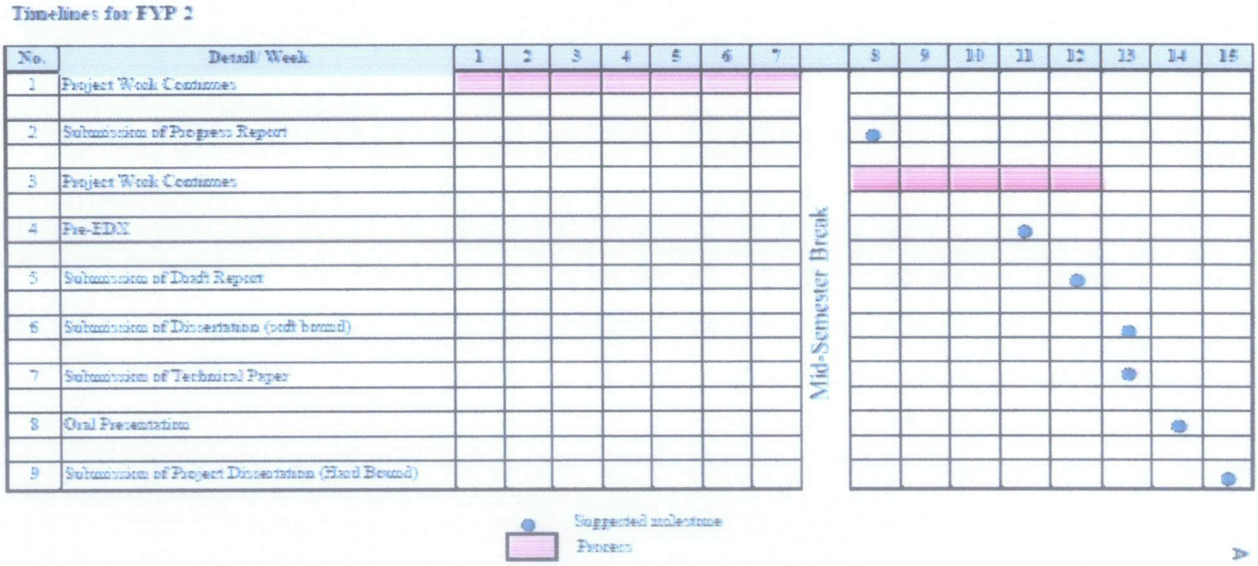


Figure 7: Key milestone

3.2 Gantt Chat

Table 3.2: Gantt Chart



Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	▨	▨	▨	▨	▨	▨	▨	Mid-Semester Break								
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

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Acidity Test of Crude Kapok Seed Oil (KSO)

It is necessary to conduct the acidity test before proceeding to the transesterification process in order to check the acid value and the percentage of Free Fatty Acid (FFA).Three tests have been performed and the value obtained for the average acid value and percentage of FFA is 11.28 mg KOH/g oil and 5.64% accordingly. In order to avoid the soap formation during transesterification, the acid value should not exceed 1%. However, since this project will apply the 1-step process (skip esterification), therefore it is expected that the presence of catalyst, Benzyltrimethyl Ammonium, will increase the product yield as well as its conversion rates regardless of the high initial acid value.

Table 5: The average acid value for the KSO

No. of titration	Acid Value (mg KOH/g oil)	Free Fatty Acid (%)
1	11.29	5.65
2	11.25	5.63
3	11.27	5.64
Average		5.64

4.2 Transesterification

For this experiment, 8 runs have been conducted in order to obtain the optimum parameter. Each run has different condition in terms of the catalyst concentration, methanol to oil ratio, temperature and the irradiation time. The oil is left for 24 hours for the separation process to to take place in a separating funnel as shown in the figure below.

Figure 1 : Separation of product after 24-hour transesterification

Once the separation is completed, the lower layer (by-product) is removed carefully and the upper layer is kept in the bottle to be analyzed accordingly. The mass of the product and by product is weighed and recorded in a table.

4.2.1 Acidity test of Kapok Oil Methyl Ester (KOME)

The acidity test of KOME is also tested for every run to find the relationship between the different parameters and the reduction of acid value. The tests were conducted twice and the average value is tabulated to be analyzed. The results are shown in the table below:

Table 6: The acid value for KOME

Sample	Acid Value			FFA (%)
	1	2	Average	
1	2.68	2.69	2.69	1.34
2	2.70	2.72	2.71	1.36
3	2.65	2.64	2.65	1.32
4	2.81	2.84	2.83	1.41
5	2.71	2.78	2.75	1.37
6	2.36	2.39	2.38	1.19
7	2.60	2.61	2.61	1.30
8	2.87	2.86	2.87	1.43

From the table, it can be seen that the average acid value is two and above but still below three. The values are relatively lower than the initial acid values but it is higher if compared with the European Biodiesel standard, EN14214 and American Standard ASTM 6751, which biodiesel should have acid value below 0.5 mg KOH/g oil. Moreover, it can be seen that the different in parameters do not have any relationships or trend with the acidity of KOME.

4.2.2 KOME Yield

The samples are then analyzed by the Gas Chromatography to obtain the yield. The results are shown in the table below:

Table 7: The FAME yield for each sample

Sample	FAME yield (%)
1	78.06
2	85.26
3	81,29
4	89.81
5	79.59
6	87.26
7	35.06
8	60.51

The FAME conversion percentage is calculated from the chromatograms obtained from Gas Chromatography as attached in the Appendix A. The internal standard used is known as Methyl Nanodecanoate. The equation is shown below:

$$C = \frac{\sum A - A_{IS}}{A_{IS}} \text{ X } \frac{C_{IS} \text{ X } V_{IS}}{m} \text{ X } 100$$

Where $\sum A$ = Total Peak Area

A_{IS} = Peak area of internal standard

C_{IS} = Concentration of internal standard (1 mg/ mL)

V_{IS} = Volume of internal standard (1 mL)

m = mass of sample

Based from the table, the highest yield is obtained for sample number 4, in which the FAME yield is 89.81% and the second one is sample number 6 for obtaining 87.26% yield. There is one major similarity between both runs, which is the methanol to oil ratio is 14:1 whereas the concentration of catalyst for run 4 is higher than run 6; 3% and 1% respectively. In terms of the temperature, sample 4 is performed under 70 deg celcius for 2 minutes whereas sample 6 is 40 degree celcius for 5 minutes.

Meng Kiat (2013) designed the same experiment and has obtained 96.6 % FAME yield with the optimum parameter of 55 degree Celcius, 2 wt% catalyst, 10:1 methanol to oil ratio and 3.5 minutes reaction time. The optimum parameters obtained for both authors are totally different and Meng Kiat has obtained higher yield of FAME.

This phenomenon is probably caused by the increased amount of Free Fatty Acids and water content in the parent oil, which negatively affected the transesterification reaction. The presence of free fatty acids makes the catalyst loss greater due to neutralization side reactions. A high consumption of catalyst means that the methanolysis remains incomplete. Moreover, another possible reason for lower FAME yield is the formation of Amides during transesterification. This mechanism is similar to the side reaction of saponification and may explained the reduced methyl ester content in KOME. Take note that Amides are perfectly soluble in the methyl ester phase and have the same physiochemical parameters with Biodiesel. Furthermore, since the oil did not undergo the esterification process, it is actually possible for these types of raw materials to contain high molecular weight species, such as polymerized acylglycerols, that is mainly formed during the thermal stressing and oxidation. These compounds will increase the polymerized esters (higher molecular weight than a monomer ester) and will eventually lower the methyl esters as they cannot be detected with the traditional test method of EN 14103.

4.2.3 The percentage yield of Biodiesel by mass

The table below shows the percentage yield of Biodiesel by mass after conducting eight runs consecutively.

Table 8: The percentage yield of Biodiesel by mass

Sample	Weight of oil (g)	Weight of Biodiesel product	Weight of byproduct (g)	Yield (%)
1	50.03	28.81	23.19	57.58
2	50.01	29.23	24.21	58.44
3	50.05	27.26	25.63	54.46
4	50.05	29.98	24.44	59.90
5	50.10	22.76	29.24	57.21
6	50.04	28.21	21.83	55.62
7	50.10	29.22	20.88	53.15
8	50.08	22.11	29.89	59.54

Based from the table above, after conducting eight runs by using different parameters in terms of the catalyst concentration, solvent amount, irradiation time and temperature, the results show average yield of biodiesel. All the eight runs show yield of an average of 55% by mass and the highest ever recorded is for run number 4; successfully obtained 59.90% of biodiesel. The parameters involved for this run is methanol to oil ratio: 14, 3 wt% of catalyst, 70 degree Celcius and 2 minutes reaction time in the microwave. Hence, these parameters are considered to be the most optimum condition to produce KOME up to this extent.

4.3 Energy consumption for Microwave

Run number 4 shows the highest yield up to the extent the report is written. Hence the irradiation time is 2 minutes to produce 59.90% KOME. A previous study (Norazhar et. Al, 2012) shows that it requires about 3 hours to produce 98% yield hence in general, it is assumed that in order to obtain approximately 60% yield, it probably takes around 1.9 hour.

The microwave reactor is customized from the domestic oven and it has the power output of 1200 Watts. Plus, it is equipped with the mechanical stirrer which consumes energy as well. For the record, the maximum energy consumed by the stirrer is 90 Watts (Meng Kiat, 2013).

Total energy consumption = 1290W x 2 min x $\frac{1\ hour}{60\ min}$ x $\frac{1\ kW}{1000W}$ = 0.043 kWh

For conventional method, Favorit stirring hot plate model HS0707V2 has the power output of 1007 Watts per used.

Total energy consumption = 1007W x 1.9 x $\frac{1\ kW}{1000W}$ = 1.910 kWh

Table 9 :Comparison of energy consumption

	Microwave heating	Conventional Heating
Energy dissipated (W)	1290	1007
Time of reaction (min)	2	114
Total Energy required (kWh)	0.043	1.910

Based from the table above, for 50 g of kapok oil to undergo transesterification, the microwave requires 0.043 kWh to yield 59.90% whereas the conventional heating is expected to require approximately 1.910 kWh for the same yield percentage. This shows significant difference in which, conventionl heating requires about 44 times energy if relatively compared to the microwave technique.

4.4 Characterization of KOME

The KOME properties produced under optimum condition is characterized and compared with the American biodiesel standard, ASTM 6751 and European standard, EN 14214.

Table 10: Properties of KOME in comparison with ASTM 6751 and EN 14214

Properties	KOME	ASTM 6751	EN 14214
Density @25 (kg/m3)	880	-	-
Cloud point	2.5	5	Not specified
Pour point	0	-15	Not specified etc
Cold Filter Plugging Point	1.5	-	Not specified etc
Oxidative stability (hr)	3.90	3 min	6 min
Acid Value (mg KOH/g oil)	2.83	<0.5	<0.5

There are three main elements in the flow of biodiesel which is the cloud point (CP) pour point (PP) and cold filter plugging point (CFPP). CP is the temperature at which dissolved solids are no longer completely soluble, where wax from biodiesel starts to form cloudy appearance. Pour point is the lowest temperature at which biodiesel becomes semi solid and losses its flow characteristics. CFPP gives the estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel system. It is mainly important for the low temperature countries which high CFPP will clog up engine easily.

The oxidative stability is analyzed by biodiesel rancimat method EN 14112. This property is the main contributor to the major problem for storage. The presence of unsaturated bonds influence the property at most.

For the acid value, it can be seen that the average acid value is reduced from 11.25 mg KOH /g oil (before transesterification) to 2.83 mg KOH / g oil. Although the average value has been decreased, it still did not meet the standard since for both standards, the requirement for the acid value is to be less than 0.5 mg KOH/ g oil.

CHAPTER 5

CONCLUSION

5.1 Conclusion

The project has been successfully completed with accordance to the objectives, in which Biodiesel is produced from Ceiba Pentandra by using 8 runs and microwave assisted technique. Moreover, in order to obtain the optimum parameters, there are 4 variables to be manipulated such as the methanol to oil ratio, temperature, catalyst concentration and irradiation time. Based from the results, the highest FAME yield (89.81%) is obtained at the methanol to oil ratio is 14:1, 3% catalyst concentration, 70 degree Celcius for 2 minutes irradiation time. Furthermore, the application of microwave technique has successfully reduced the reaction time as well as the total energy consumption for the transesterification process. Lastly, the properties of the FAME produced under the optimum parameters are characterized by using the international standard of Biodiesel (ASTM 6751 & EN 14214). It can be seen that some of the FAME properties obtained are comparable to both standards (oxidative stability) whereas some did not meet the standard so far (acid value). It can be said that the modification of the experiment in terms of the 1-step transesterification and the introduction of Benzyltrimethyl Ammonium is giving significant effects towards the production of Biodiesel especially the maximum yield (89.81%). However, more studies and researches should be conducted to improve the results and to ensure that all properties of Biodiesel will meet the standard of ASTM 6751 and EN 14214.

5.2 Recommendation

The esterification and transesterification of kapok seed oil should be scaled down to less than 30g of raw material. However, one of the major drawbacks of laboratory equipment is the scale of the 3-neck round bottom; a maximum allowable volume of 500mL only. Hence, it is suggested to scale down the experiment work to avoid the excessive evaporation of methanol solvent into the atmosphere and causing inaccuracy in results. Plus, based form the previous research (Meng Kiat, 2013) the acidity of the kapok seed oil or biodiesel should be tested at regular basis, for instance once in a week. The main reason is the acidity of the oil tends to increase by time. Thus, more accurate results and analysis can be achieved by monitoring the oil more frequently.

5.3 Future Work

After the project has been completed, few issues have been highlighted in order to obtain more accurate and precise results in the future. Firstly, it is suggested to do more massive researches on the parameters involved; solvent to oil ratio, catalyst concentration, temperature and irradiation time. This is due to the fact that the it is actually possible for the parameters to be interconnected to each other thus resulting the yield or characteristic of Biodiesel. Moreover, another crucial aspect that should be taken into account is the kinetic of the processes involved especially transesterification. By doing so, the reaction rate can be determined and it might be very useful for commercialization of Biodiesel in the future.

REFERENCES

Yusup, S., & Khan, M. (2010). Basic properties of crude rubber seed oil and crude palm oil blend as a potential feedstock for biodiesel production with enhanced cold flow characteristics. *Biomass and Bioenergy* , 34:1523-1526.

Srivastava, A., & Prasad, R. (2000). Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews* , 4:111-133.

Mundi, I. (n.d.). Citing Websites.Malaysia - Road sector diesel fuel consumption. Retrieved June 27, 2013, from http://www.indexmundi.com/facts/malaysia/road-sector-diesel-fuel-consumption

Leadbeater, N. E., & Stencel, L. M. (2006). Fast, easy preparation of biodiesel using microwave heating. *Energy & Fuel* , 2281-2283.

Kumar, R., Kumar, G. R., & Chandrashekar, N. (2011). Microwave assited alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. *Bioresource Technology* , 6617-6620.

Ye, J., Tu, S., & Sha, Y. (2010). Investigation to biodiesel production by the two-step homogeneous base-catalyzed transesterification. *Bioresource Technology* ,101:7368-7374.

A.S. Ramadhas, S. Jayaraj & C. Muraleedharan (2005). Biodiesel production from high FFA rubber seed oil, *84*(4), 335-340 http://www.sciencedirect.com/science/article/pii/S0016236104002844

Knothe, G. (2007). Some aspects of biodiesel oxidative stability. *Fuel Process Technol*88:66677

.

Yan, S., Kim, M., Salley, S. O., & Ng, K. Y. (2009). Oil transesterification over calcium oxides modified with lanthanum. *Applied Catalyst A: General* , 360:163-170.

Yaakob, Z., Sukarman, I. S., Kamarudin, S. K., Mohamed, F., & Abdullah, S. R. (2008). Production of biodiesel from jatropha curcas by microwave irradiation. *International Conference on Renewable Energy Sources, Corfu, Greece* , 235-239

Clark, J. (n.d.). Citing Websites.Esterification. Retrieved June 127, 2013, from http://www.chemguide.co.uk/organicprops/alcohols/esterification.html

Walia, Y. K., Kishore, K., Vasu, D., & Gupta, D. K. (2009). Physico-chemical analysis of Ceiba pentandra (Kapok). *Int J Theor Appl Sci* , 1:15-18.

Tye, Y. Y., Lee, K. T., N., W. A., & Leh, C. P. (2012). Potential of Ceiba pentandra (L.) Gaertn (kapok fiber) as a resource for second generation bioethanol: effect of varios simple pretreatment methods on sugar production. *Bioresour Technol* , 116:536-539.

T. Michael Barnard and Nicholas E. Leadbeater (2007, October. Microwave Technology and Continuous-Flow Production. Retrieved from http://www.biodieselmagazine.com/articles/1865/microwave-technology-and-continuous-flow-production/

Thamsiriroj, T., & Murphy, J. D. (2010). How much of the target for biofuels can be met by biodiesel generated from residues in Ireland? *Fuel* , 89:3579-3589

Su Zhang, Yuan-Gang Zu et. al (2010). Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst, *101*(3), 931-936. http://www.sciencedirect.com/science/article/pii/S0960852409011328

Sivakumar, P., Sindhanaiselvan, S., Ghandi, N. N., Devi, S. S., & Renganathan, S. (2013). Optimization and kinetic studies on biodiesel production from underutilized Ceiba Pentandra Oil. *Fuel* , 103:693-698.

Z. Helwani, M.R. Othman et. al (2009). Technologies for production of biodiesel focusing on green catalytic techniques: A review, *90*(12), 1502-1514. http://www.sciencedirect.com/science/article/pii/S0378382009002148

Sinha, S., Agarwal, A. K., & Garg, S. (2008). Biodeisel development from rice bran oil: transesterification process optimization and fuel characterization. *Energy Conversion and Management* , 49:1248-1257.

Nicholas E. Leadbeater, T. Michael Barnard et. al (2005-2008). Batch and Continuous-Flow Preparation of Biodiesel Derived from Butanol and Facilitated by Microwave Heating, *22*(3). http://pubs.acs.org/doi/abs/10.1021/ef700748t

Sherbiny, S. A., Refaat, A. A., & Sheltawy, S. T. (2010). Production of biodiesel using the microwave technique. *Journal of Advance Research, vol. 1* , 309-314.

Bernhard Neises, Prof. Dr. Wolfgang Steglich (2003). Simple Method for the Esterification of Carboxylic Acids, *17*(7), 522-524. http://onlinelibrary.wiley.com/doi/10.1002/anie.197805221/abstract

Serio, M. D., Tesser, R., Pengmei, L., & Santacesaria, E. (2008). Heterogeneous catalyst for biodiesel production. *Energy and Fuels* , 22:207-210.

Peterson, C. L., Feldman, M et. al (1991). Batch type transesterification process for winter rape oil., *7*(6), 711-716. http://www.cabdirect.org/abstracts/19922452113.html;jsessionid=FD1933168E1C9E3C8E656A79B1CCBE64;jsessionid=B5BE2E24E5289A0052B42F70DE7BD184

Salimon, J., & Kadir, K. A. (2005). Fatty acid composition and physicochemical properties in kekabu seed oil. *Sains Malaysiana* , 34(2):117-120.

Reefat, A. A., Sheltawy, S. T., & Sadek, K. U. (2008). Optimum reaction time, performance and exhaust emissions of biodiesel produced by microwave irradiation. *International journal of Environmental Science and Technology* ,5:315-322.

Xin Deng, Zhen Fang et. al (2010). Ultrasonic transesterification of *Jatrophacurcas* L. oil to biodiesel by a two-step process, *51*(12), 2802-2807. http://www.sciencedirect.com/science/article/pii/S0196890410002293

Ramadhas, A., Jayaraj, S., & Muraleedharan, C. (2003). Chemical composition and nutritive value of kapok seed meal for broiler chickens. *British Poultry Sci* ,4:505-509.

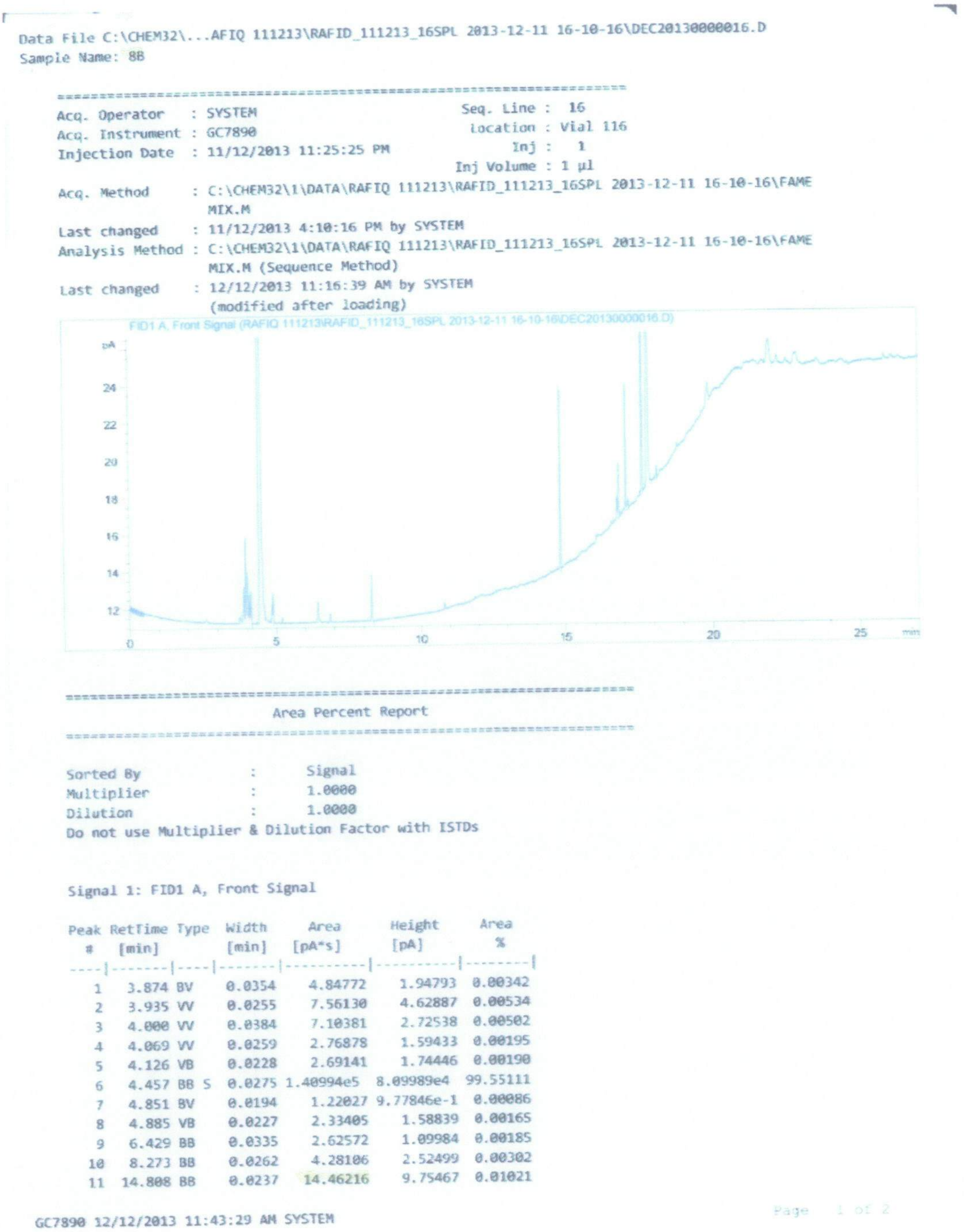
Meher, L. C., Sagar, D. V., & Naik, S. N. (2006). Technical aspects of biodiesel production by transesterification - a review. *Renewable and Sustainable Energy Reviews* , 248-268.

Leung, D. Y., Wu, X., & Leung, M. K. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy* , 87:1083-1095.

Lersathapornsuk, V., Pairintra, R., Krisnangkura, K., & Chindaruksa, S. (2003). Direct conversion of used vegetable oil to biodiesel and its use as an alternative fuel for compression ignition engine. *1st International Conference on Energy and Green Architecture.*

APPENDICES

Appendix 1: Example of Gas Chromatography 1



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                                                     Inj Volume : 1 µl
    Acq. Method      : C:\CHEM32\1\DATA\RAFIQ 111213\RAFID_111213_16SPL 2013-12-11 16-10-16\FAME
                       MIX.M
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                          Area Percent Report
    =====================================================================

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    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A, Front Signal

    Peak RetTime Type  Width      Area      Height     Area
      #   [min]        [min]    [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   3.874 BV    0.0354    4.84772    1.94793  0.00342
       2   3.935 VV    0.0255    7.56130    4.62887  0.00534
       3   4.000 VV    0.0384    7.10381    2.72538  0.00502
       4   4.069 VV    0.0259    2.76878    1.59433  0.00195
       5   4.126 VB    0.0228    2.69141    1.74446  0.00190
       6   4.457 BB S  0.0275 1.40994e5 8.09989e4  99.55111
       7   4.851 BV    0.0194    1.22027 9.77846e-1  0.00086
       8   4.885 VB    0.0227    2.33405    1.58839  0.00165
       9   6.429 BB    0.0335    2.62572    1.09984  0.00185
      10   8.273 BB    0.0262    4.28106    2.52499  0.00302
      11  14.808 BB    0.0237   14.46216    9.75467  0.01021

GC7890 12/12/2013 11:43:29 AM SYSTEM                                      Page  1 of 2
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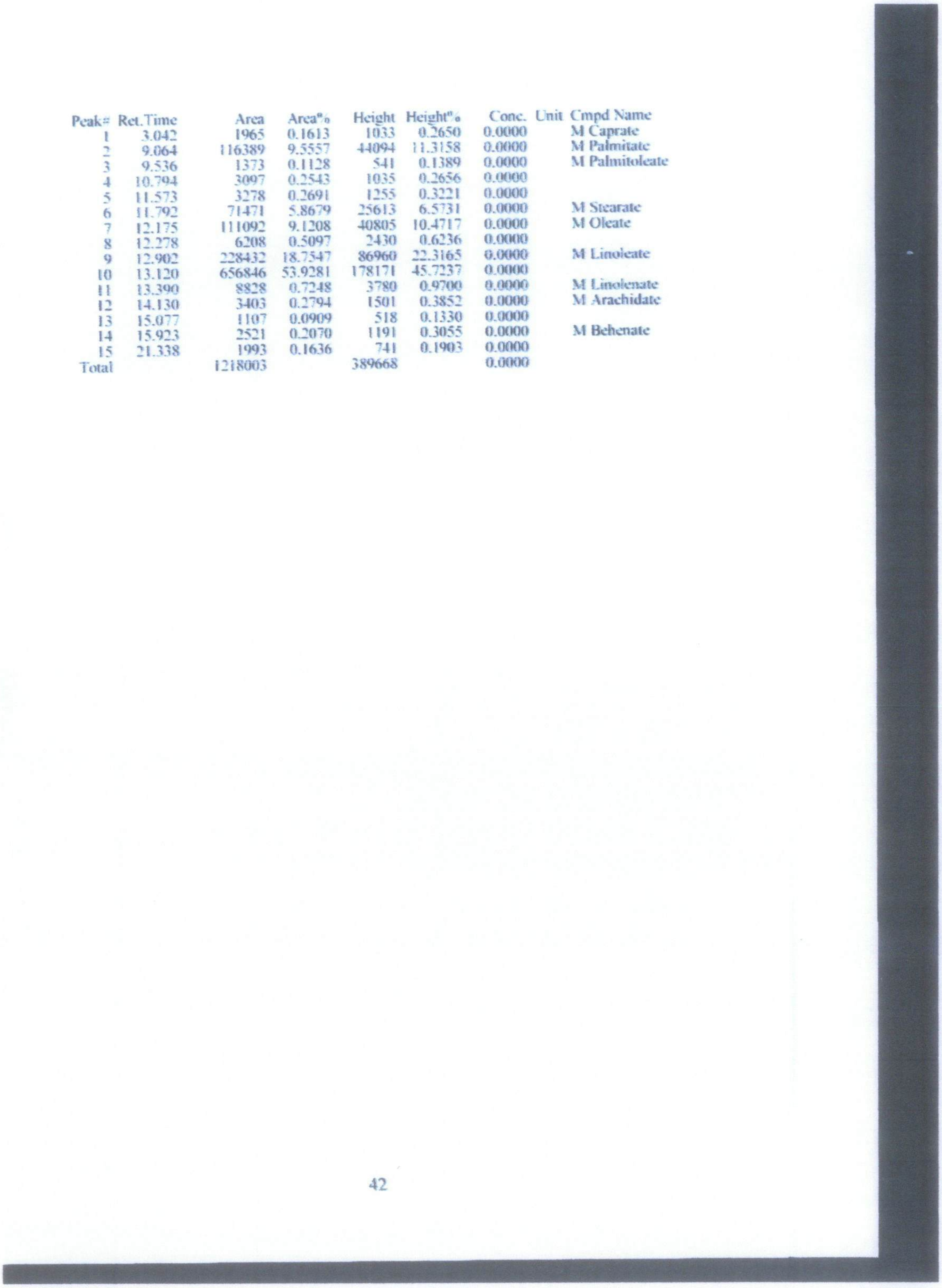

Peak#	Ret.Time	Area	Area%	Height	Height%	Conc.	Unit	Cmpd Name
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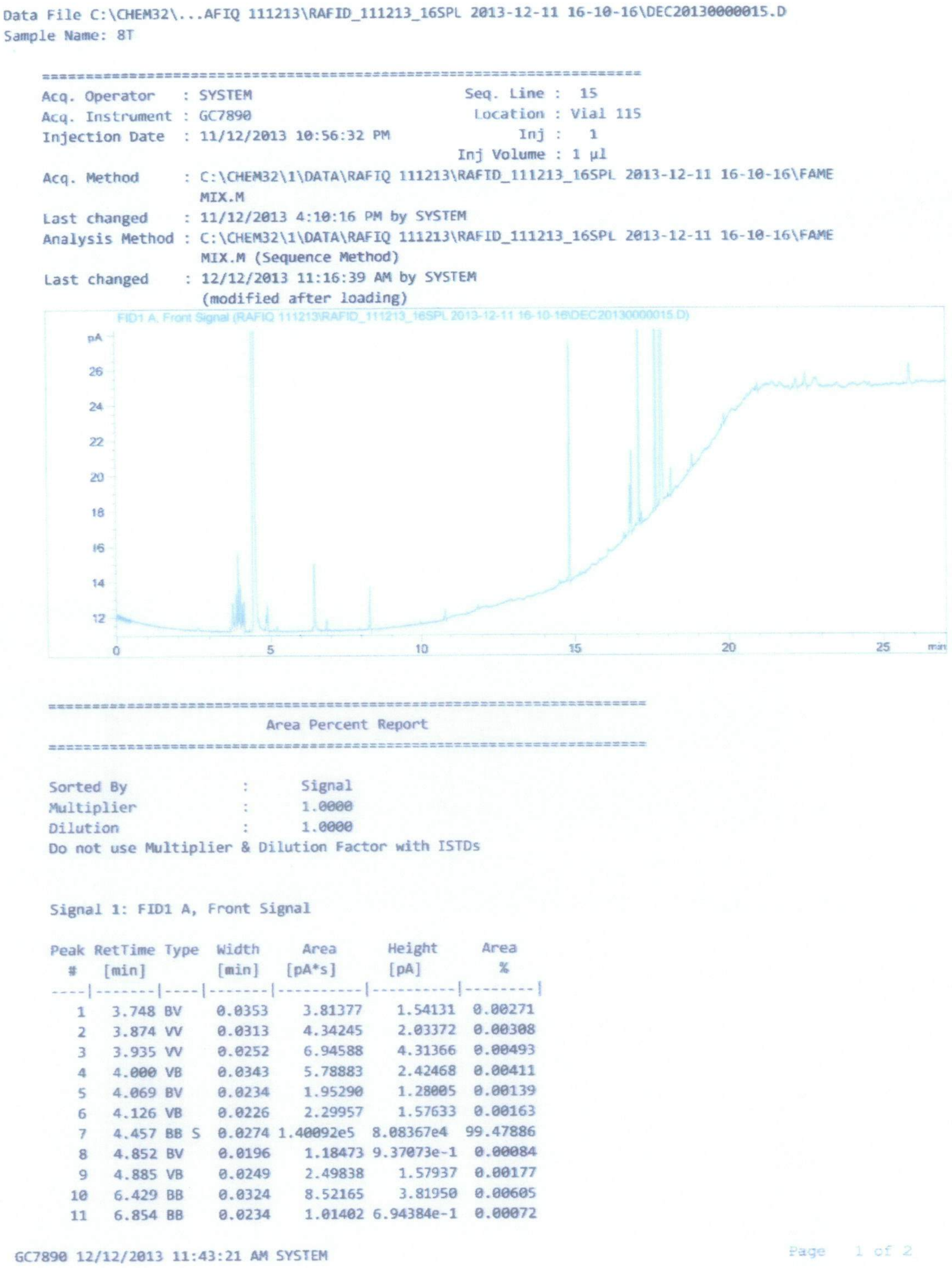
2	9.064	116389	9.5557	44094	11.3158	0.0000		M Palmitate
3	9.536	1373	0.1128	541	0.1389	0.0000		M Palmitoleate
4	10.794	3097	0.2543	1035	0.2656	0.0000		
5	11.573	3278	0.2691	1255	0.3221	0.0000		
6	11.792	71471	5.8679	25613	6.5731	0.0000		M Stearate
7	12.175	111092	9.1208	40805	10.4717	0.0000		M Oleate
8	12.278	6208	0.5097	2430	0.6236	0.0000		
9	12.902	228432	18.7547	86960	22.3165	0.0000		M Linoleate
10	13.120	656846	53.9281	178171	45.7237	0.0000		
11	13.390	8828	0.7248	3780	0.9700	0.0000		M Linolenate
12	14.130	3403	0.2794	1501	0.3852	0.0000		M Arachidate
13	15.077	1107	0.0909	518	0.1330	0.0000		
14	15.923	2521	0.2070	1191	0.3055	0.0000		M Behenate
15	21.338	1993	0.1636	741	0.1903	0.0000		
Total		1218003		389668		0.0000		

Appendix 2: Example of Gas Chromatography 2



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                           Area Percent Report
     =====================================================================

     Sorted By             :      Signal
     Multiplier            :      1.0000
     Dilution              :      1.0000
     Do not use Multiplier & Dilution Factor with ISTDs


     Signal 1: FID1 A, Front Signal

     Peak RetTime Type  Width     Area      Height     Area
       #   [min]        [min]   [pA*s]      [pA]        %
     ----|-------|----|-------|----------|----------|--------|
        1   3.748 BV    0.0353    3.81377    1.54131  0.00271
        2   3.874 VV    0.0313    4.34245    2.03372  0.00308
        3   3.935 VV    0.0252    6.94588    4.31366  0.00493
        4   4.000 VB    0.0343    5.78883    2.42468  0.00411
        5   4.069 BV    0.0234    1.95290    1.28005  0.00139
        6   4.126 VB    0.0226    2.29957    1.57633  0.00163
        7   4.457 BB S  0.0274 1.40092e5  8.08367e4  99.47886
        8   4.852 BV    0.0196    1.18473 9.37073e-1  0.00084
        9   4.885 VB    0.0249    2.49838    1.57937  0.00177
       10   6.429 BB    0.0324    8.52165    3.81950  0.00605
       11   6.854 BB    0.0234    1.01402 6.94384e-1  0.00072

GC7890 12/12/2013 11:43:21 AM SYSTEM                                      Page   1 of 2
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    Peak RetTime Type  Width     Area      Height     Area
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    ----|-------|----|-------|----------|----------|--------|
      12  16.755 BV    0.0264    2.12407    1.18933 0.00150
      13  16.805 VB    0.0269    4.89046    2.89864 0.00345
      14  17.051 BV    0.0282   12.68214    6.77562 0.00895
      15  17.128 VB    0.0323    1.12566 5.07020e-1 0.00079
      16  17.588 BB    0.0259   22.41004   13.43147 0.01582
    99 17  17.800 BB    0.0328  528.07080  240.76292 0.37285
      18  18.093 BB    0.0294    1.17058 6.15240e-1 0.00083
      19  19.836 BB    0.0607    4.94751    1.06336 0.00349
      20  21.900 BB    0.0836    8.44638    1.27621 0.00596

    Totals :                   1.41629e5  8.12960e4

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