EXTRACTIVE REACTION OF BIODIESEL SYNTHESIS USING ETHANOL AS A SOLVENT: A CONVERSION STUDY

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EXTRACTIVE REACTION OF BIODIESEL SYNTHESIS USING ETHANOL AS A SOLVENT: A CONVERSION STUDY

NORHARTINI BINTI KASSIM

Thesis submitted in fulfilment of the requirements
for the award of the degree
in Bachelor of Chemical Engineering

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duty acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Special dedication to my mum, dad, brothers and sister that always inspire, love and stand beside me,
and also to my beloved friend.

Thank you for all your love, care and support.

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ABSTRACT

Worldwide high demand for energy, uncertainty of petroleum resources and concern about global climatic changes has led to the resurgence in the development of alternative liquid fuels. Ethanol has always been considered a better choice as it reduces the dependence on crude oil and promises cleaner combustion leading to a healthier environment. Developing ethanol as fuel beyond its current role of fuel oxygenate, would require lignocelluloses as a feedstock because of its renewable nature, abundance and low cost. Nevertheless, in most of the studies, methanol was used as the reaction and extraction medium. The use of methanol deviate the purpose of producing renewable energy since methanol is mostly derived from fossil fuel. Therefore in this study, the use of ethanol as the extraction and reaction medium for biodiesel synthesis to produces FAEE was investigated. The objective of this research is to determine the effect varying extraction rate on the biodiesel production by extractive reaction from palm oil using ethanol as a solvent. The experimental procedure to produce biodiesel consist of 2 major experiment which were control experiment and extractive reaction experiment. Operating condition is at 60 ˚C of temperature with molar ratio of ethanol to oil is 6:1 was fixed. The study shows, the extractive rate on the conversion of ethanol in biodiesel synthesis was improved by the extraction system. As a conclusion, ethanol have a better oil extraction property by applying the extractive reaction.

Keywords: Extractive Reaction, Biodiesel, Ethanol as a solvent, Free Fatty Acid Ethyl Ester (FAEE)

ABSTRAK

Permintaan yang tinggi di seluruh dunia untuk sumber tenaga adalah semakin memberangsangkan, tetapi kekurangan sumber petroleum dan kebimbangan mengenai perubahan iklim global telah membawa kepada kebangkitan semula dalam pembangunan bahan api cecair alternatif. Etanol telah dianggap sebagai pilihan yang lebih baik kerana ia mengurangkan pergantungan kepada bahan api mentah, menjanjikan pembakaran yang bersih dan membawa kepada persekitaran yang lebih sihat. Mengolah etanol sebagai bahan api di luar peranannya yang sebenar sebagai bahan api oksigen adalah langkah yang bijak kerana etanol boleh terhasil daripada kanji yang boleh didapati dari alam semula jadi. Ia adalah bahan mentah yang boleh diperbaharui, dan kos penghasilan yang rendah. Namun begitu, dalam kebanyakan kajian, metanol telah digunakan sebagai bahan tindak balas dan medium pengekstrakan. Penggunaan metanol menyimpang tujuan menghasilkan tenaga yang boleh diperbaharui oleh kerana metanol kebanyakannya berasal daripada bahan api fosil. Kajian ini dibuat, khusus kepada penggunaan etanol sebagai pengekstrakan dan medium tindak balas untuk menghasilkan biodiesel. Objektif kajian ini adalah untuk menentukan kesan pengekstrakan pada kadar yang berbeza untuk pengeluaran biodiesel oleh tindak balas ekstraktif daripada minyak sawit menggunakan etanol sebagai bahan pelarut. Langkah-langkah kajian untuk menghasilkan biodiesel terdiri daripada dua kajian utama, yang pertama ialah eksperimen kawalan dan yang kedua eksperimen tindak balas ekstraktif. Tindak balas kajian beroperasi pada suhu 60˚C dengan nisbah molar etanol kepada minyak 6:1 telah ditetapkan. Kajian menunjukkan, kadar ekstraktif pada penukaran etanol dalam sintesis biodiesel telah bertambah kepada lebih baik oleh sistem pengekstrakan. Sebagai kesimpulan, etanol mempunyai perahan minyak yang lebih baik dengan menggunakan tindak balas ekstraktif.

Kata Kunci: Tindak balas ekstraktif, Biodiesel, Ethanol sebagai pelarut, Asid Lemak Ethyl Ester (FAEE)

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LIST OF ABBREVIATIONS & SYMBOLS

%	Percentage
FAEE	Fatty Acid Ethyl Ester
CH_4OH	Ethanol
Al_2O_3	Aluminium Oxide
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
DMAP	Dimethylaminopyridine
FFA	Free Fatty Acid
TG	Triglyceride
GC	Gas Chromatography
GC-FID	Gas Chromatography-Flame Ionized Detector
DRF	Detector Response Factor
˚ C	Degree Celsius

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Currently, biodiesel has received attention, as petroleum prices and concern for the environment have increased. Biodiesel can be used with little or no modifications to existing diesel engines, and has a low emissions profile (BiodieselNow, 2006). Biodiesel has lower emissions than regular diesel and does not contribute to an increase in carbon dioxide in the atmosphere since all the material comes from plants, and extends the life of the engine due to its good lubricity. Biodiesel is a renewable fuel derived from vegetable oils and animal fats that can be used in diesel engines. Though biodiesel reduces hazardous emissions, other environmental factors such as land cultivation and competition with agricultural products for human consumption make biodiesel more of a short term alternative energy.

The possibility of using vegetable oils as fuel has been recognized since the beginning of Diesel engines. Vegetable oil has too high a viscosity for use in most existing Diesel engines as a straight replacement fuel oil. There are a number of ways to reduce the viscosity of the vegetable oil. Dilution, micro-emulsification, pyrolysis and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. Chemical conversion of the oil to its corresponding fatty ester is called transesterification. (Bala, 2005). **Figure 1** shows the transesterification reaction of triglicerides.

$3C_2H_5OH$ + Triglyceride ↔ 3FAEE + Glycerol
(Ethanol) (Fatty Acid Ethyl Ester)

Figure 1.0: Transesterification of triglyceride with alcohol to form biodiesel

One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol (methanolysis) to make methyl esters of the straight chain fatty acid. However, this makes the biodiesel produced not 100% renewable since methanol is a fossil-fuel base product. Besides, ethanol which was reported to have better oil extraction solvent due to its longer alkyl chain and less polarity as compared to methanol in which the non-polar oil will be more easily dissolved so ethanol is good to overcome the limiting factor in reactive extraction process (Lee C.G, 2000).

The biodiesel reaction requires a catalyst such as potassium hydroxide (KOH)/ sodium hydroxide (NaOH) to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. The main byproduct is glycerin. The process reduces the viscosity of the end product. Transesterification is widely used to reduce vegetable oil viscosity (Pinto AC, 2005).

1.2 Problem Statement

The biodiesel synthesis involves multiphase that may render mass transfer effects to be significant. Extraction is one of the potential methods in separating reactors that can be used to improve the reaction yield. In particular, a liquid-liquid system of extraction is favorable due to the low temperatures window of the transesterification reactor of edible or non-edible oil with short chain alcohols such as ethanol and methanol. The liquid-liquid extraction is a controlled mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly immiscible liquid. Biodiesel production in Malaysia is apparently practical to the use of non-edible oils and palm oil as the feedstock. Biodiesel that is available in the market is currently produced using methanol as the source of alcohol. However, this makes the biodiesel produced not 100% renewable since methanol is a fossil-fuel base product. Moreover, using methanol as alcohol source in biodiesel production will lead to uncertainty in product cost and supply since fossil sources in the world are now depleting (Gui M.M., Lee K.T. and Bhatia S;, 2009). Therefore, using ethanol which can be derived from renewable sources such as lignocelluloses material as alcohol source would be a potential solution to overcome this limitation. Besides, ethanol which was reported to have better oil extraction property (Lee C.G., 2000) is additionally expected to be able to overcome the limiting factor in reactive extraction process by means of simultaneously-continuous extraction (Shuit S.H., 2010). When ethanol is employed, fatty acid ethyl esters (FAEE) will be obtained as the products of the transesterification reaction while the alcohol extracting the product from the oil phase where the reaction occurs. Thus the aim of this study is to study the phenomena of extractive reaction using ethanol as alcohol source for the production of biodiesel from palm oil (Venice, 2010).

1.3 Objective

The purpose of this thesis is:

- To determine the effect varying extraction rate on the biodiesel by including proper rate of reactant and solvent.

- To characterizes and assess the efficiency of using ethanol as a solvent.

1.4 Scope of the research work

In order to achieve the target, extra effort and focus have to be done with the topic of extractive reaction of biodiesel synthesis using ethanol as a solvent

- The reaction temperature is between 60°C-70°C
- The identification components of oil and ethanol is analyze by Gas Chromatography

1.5 Rationale & Significance of Study

This studies was been carried out to synthesize and develop the phenomena of extractive reaction using ethanol as alcohol source for the production of biodiesel from palm oil:

- Triglyceride source is palm oil : readily available vegetable oil in Malaysia
- New technique in producing biodiesel with less unit operations and heat loss.
- Analyze the small-scale reactions to serve as a model for industrial production.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The biodiesel is a mixture of methyl or ethyl esters of fatty acids that can be used as a fuel for diesel engines. The ester group increases the oxygen content of diesel-biodiesel blends improving the efficiency of the combustion of the conventional fossil diesel. For producing biodiesel, the transesterification of vegetable oils with low molecular weight alcohols like methanol or ethanol is necessary. This reaction is accomplished with the help of acid, basic or enzymatic catalysts. Usually, biodiesel production in the world is carried out employing methanol and basic catalysts (mostly KOH). The most employed vegetable oils are rapeseed, soybean and sunflower oils. The oil from palm (*Elaeis guineensis*) is considered as an excellent feedstock for biodiesel production in tropical countries. The conventional technologies for biodiesel production employ reactors with acid or basic catalysts and a separation scheme that uses unit operations like distillation, centrifugation, flash evaporation, filtration, and decantation. The purification of this biofuel through the operation mentioned implies high capital investment and energy consumption leading to elevated production costs. Process design trends in chemical industry are related to the development of more efficient technologies. One of the most important approaches for the design of more intensive and cost-effective process configurations is process integration, which looks for the integration of all operations involved in the production of one specific product. This can be achieved through the development of integrated processes that combine different steps into one single unit. The reactive extraction is an integrated process simultaneously combining the chemical reaction and liquid-liquid extraction. The latter phenomenon allows the continuous removal of the reaction products favouring the direct conversion in the case of reversible reactions like the esterification of vegetable oils with methanol. The objective of this work is to evaluate the possibility of applying the integration principle to the biodiesel production from palm oil by extractive reaction. (Gutiérrez L. F, 2010)

2.2 Catalyst

Catalyst is a substance for change in rate of a chemical reaction. A catalyst may participate in multiple chemical transformations. Promoter is a substance that increasing the reactivity of catalyst while catalytic poisons is a substance that deactivated catalyst. Catalyst divided by heterogeneous catalyst and homogeneous catalyst. Heterogeneous catalysts such as Palladium on activate charcoal used in the reaction of hydrogen with nitro groups to produce amine groups. Homogeneous catalyst such as DMAP (dimethylaminopyridine) used in solution to catalyst esterification reactions.

2.3 Homogeneous Catalyst

(G. Vicente et al., 2003) studied a comparison of different homogeneous catalyst system (Integrated biodiesel production). A comparison is made of different basic catalyst which is sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide for methanolysis of sunflower oil. In their findings, the methyl ester concentrations were near 100wt% when used four catalysts. For the methoxide catalysts, biodiesel yields were higher than 98wt% after the separation and purification step while biodiesel yields for sodium and potassium hydroxide were lower namely 85.9 and 91.67 wt%. The biodiesel yields can be higher when a modification of the value for experimental conditions such as temperature and catalyst concentration.

(D. A. G. Aranda et al., 2007) studied the acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. In this experiment, used different of homogeneous catalyst such as sulfuric acid, methanesulfonic acid, phosphoric acids were the best catalysts. In their findings, sulfuric and methanesulforic acids were the best catalyst, with conversion higher than 90% at 1 h of reaction for reactant methanol and ethanol. For different alcohols, methanol reaction was faster than ethanol. For effect of water in the reaction medium, inhibition effect can be found in the ethanol reaction. A small amount of catalyst (0.01 w/w) is enough to promote the reaction.

(T. Joseph et al., 2005) studied a green, efficient and reusable catalyst system and reaction medium for Fischer esterification by bronsted acidic ionic liquids. Bronsted acidic ionic liquid containing nitrogen based organic cation 1-methylimidazole and 1-buthyl-3-methylimidazolium and inorganic anions of the type BF4, PF6 and PTSA. In their findings, a maximum 100% conversion and 100% product selectivity was obtained on using PTSA as catalyst over a period of 2 h. For PF6 used in the reaction also gave 100% conversion in 2 h but only 90% selectivity for ester was achieved. In the effect of mole ratio of imidazole and BF4 that on increasing the amount of anion in the ionic liquid, the conversion increases but the selectivity remains the same. The reaction had to be carried out for longer time for complete conversion. When the temperature was increase to 120°C, the conversions also increase.

(B. Tosh et al., 2000) studied the homogeneous esterification of cellulose in the lithium chloride-N, N-dimethylacetamide solvent system: effect of temperature and catalyst. In their findings, LiCL-DMAc was found to be an excellent solvent system for the acetylation of cellulose with acetic anhydride in the presence of p-TsCL or pyridine. Pyridine is more active as a catalyst for esterification than p-TsCL. In case of esterification with higher anhydrides, p-TsCL might serve as a better catalyst.

(M. Di Serio et al., 2005) studied the synthesis of biodiesel via homogeneous Lewis acid catalyst. In their finding, bivalent cations are catalyst for both transesterification and esterification reactions. Catalytic activities are related to the Lewis acid strength of the metals and to the molecular structure of the anion a complex. The best catalytic performances were obtained with cation metals having stability constant with dibenzoilmetane in the range between 8.60 (corresponding to cadium) and 10.23 (corresponding to zinc). Then, the stearates have better performances than acetates.

2.4 Heterogeneous Catalyst

Heterogeneous catalyst was present in a different phase, usually in solid phase. Heterogeneous catalyst has many advantages that main advantage is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes. Heterogeneous catalyst was typically more tolerance of extreme operation condition. It is to be select for this experiment.

(J.M. Marchetti et al., 2006) studied the heterogeneous esterification of oil with high amount of free fatty acids. In their experiment, basic resin was use as a heterogeneous catalyst. In their findings, the final conversion follows an endothermic behavior when temperature is changes. Resin should be added during the process at initial FFA amounts changes to increase the final conversion. On the amount catalyst, when more catalyst is added a little higher reaction rate is achieved. In the resin is reused, the final conversion is achieved for 2nd, 3rd, and 4th reuse was less than 25%. They conclude that the resin should to be regenerated after each process and resins are a heterogeneous catalyst is appropriate to perform the esterification with higher conversion.

(H. Joo Kim et al., 2004) studied the transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. In their experiment, Na/NaOH/γ-Al_2O_3 is use for heterogeneous base catalyst. In their finding, the activities of the heterogenous base catalysts correlated with their basic strengths. *n*-hexane was the most effective with a loading amount of 5:1 VO to *n*-hexane molar ratio when the co-solvent tested. The ratio optimum methanol to oil loading was found to be 9:1. For different catalyst, the Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst showed almost the same activity under optimized reaction condition compared to the homogeneous NaOH catalyst.

(F. T. Sejidov et al., 2005) studied the esterification reaction using solid heterogenous acid catalyst under solvent-less condition. In their finding, esterification reaction of phthalic anhydride by 2-ethylexanol in the presence of solid acidic catalyst have been investigated under solvent-less condition. For the best reactivity and efficiency among the investigated heterogenous catalyst is sulfated zirconia. These catalysts are environmentally friendly and cleaner than homogeneous catalyst.

(Y. Moo Park et al., 2008) studied the heterogenous catalyst system for the continuous conversion of free fatty acid in used vegetable oils for the production of biodiesel. In their finding, the SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be effective in the esterification of free fatty acid to FAME. When the properties of the catalyst are different, it is difficult to compare batch reaction with packed-bed reactions. Packed-bed reactions have advantages over batch reactions in terms of mass production but have some disadvantages when their activity is considered. For maximize the activity of the catalyst, the optimization of the catalyst pellet size will be needed. For the characterization, the oxidation state of W is mainly related to the catalytic activity of WO_3/ZrO_2.

Table 2.1: Summary for the Homogeneous Catalyst

Author	Reaction	Catalyst	Finding
G. Vicente et al., (2003)	Esterification (Biodiesel production from sunflower oil)	Sodium Methoxide, Potassium Methoxide, Sodium Hydroxide and Potassium Hydroxide	Biodisel yields were higher when used Methoxide catalyst.
D. A. G. Aranda et al., (2007)	Esterification (Biodiesel production from Palm Fatty Acid)	Sulfuric Acid, Methanesulfonic Acid, phosphoric Acid and Trichloroacetic	Sulfuric and Methanesulfonic Acids were the best catalyst.

		Acid	
T. Joseph et al., (2005)	Esterification (Acetic acid with Benzyl Alcohol)	Bronsted Acidic ionic liquid (BF4, PF6 and PTSA)	PTSA is the best catalyst than BF4 and PF6.
B. Tosh et al., (2000)	Esterification (Cellulose in the lithium chloride–*N*,*N*-dimethylacetamide solvent system)	*p*-TsCL and Pyridine	Pyridine is more active as a catalyst for esterification than *p*-TsCL.
M. Di Serio et al., (2005)	Transesterification and Esterification (Triglycerides (TG) with Methanol)	Lewis Acid catalyst	The best catalytic performances were obtained with cation metals having stability constant.

Table2.2: Summary for Heterogeneous Catalyst

Author	Reaction	Catalyst	Finding
J. M. Marchetti et al., (2006)	Esterification (Oil with high amount of free fatty acids)	Basic resin	The basic resin is the best catalyst for esterification reaction.
H. Joo Kim et al., (2004)	Transesterification (Vegetable oil to biodiesel using heterogenous base catalyst)	$Na/NaOH/\gamma\text{-}Al_2O_3$	$Na/NaOH/\gamma\text{-}Al_2O_3$ heterogenous base catalyst showed almost the same activity.

F. T. Sejidov et al., (2005)	Esterification (Phthalic Anhydride by 2-Ethylhexanol)	Sulfated Zirconia	Sulfated Zirconia is the best reactivity and efficiency.
Y. Moo Park et al., (2008)	Esterification (Oleic Acid with Methanol)	SO_4/ZrO_2 and WO_3/ZrO_2	The SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be affective in the esterification of free fatty acid to FAME

2.5 Biodiesel Production

Main feedstock for biodiesel production analyzed in this work is palm oil that is a mixture of triglycerides. The overall process for biodiesel production comprises the following steps: feedstock conditioning, reaction, separation, and product purification. During feedstock conditioning, the content of water and free fatty acids in the vegetable oil should be controlled in order to avoid undesirable reactions and products (soap). Thus, the conditioning strongly depends on the extraction method of the vegetable oil and on its origin. The reaction step includes the transesterification reaction between the triglycerides of the oil and low molecular weight alcohols (methanol or ethanol) in the presence of a catalyst (homogeneous or heterogeneous) to form fatty esters (biodiesel) and glycerol.

The transesterification comprises three successive reversible reactions in which each one of the fatty acids linked to glycerol are to be esterified. The first step is the conversion of the triglycerides into diglycerides followed by the conversion of the diglycerides into monoglycerides and, finally, the conversion of the monoglycerides into glycerol producing one molecule of the ester per each glyceride in each step. The main products are the esters of the fatty acids (biodiesel) and glycerol. Due to the reversible character of this reaction, an excess of alcohol is employed to increase to a decanter where two liquid phases are separated: biodiesel-enriched and glycerol-enriched phases. In general, for acid and alkaline processes, neutralization of the catalyst in each phase is needed after biodiesel separation in order to form salts that could be removed afterwards. After neutralization, the biodiesel phase undergoes washing with hot water to remove the salts and the non-separated glycerol. The glycerol is dried by distillation or flashing. If economically viable, the glycerol is refined to obtain a valuable co-product.

The application of extractive reaction is one of the integration approaches that can be utilized for the intensification of biodiesel production. This process consists in the combination of the chemical reaction and liquid-liquid extraction in the same unit achieving such synergistic effect, that the increase of selectivity, conversion, productivity, and purity of final product may be attained (Rivera and Cardona, 2004). Thus, two liquid phases are formed during the reaction. In this way, the principle of reaction-separation integration can be applied to the production of ethyl esters using palm oil and even castor oil. Biodiesel-enriched liquid phase is removed from the reactor-extractor and sent to a flash unit where ethanol is recovered. In order to obtain a high purity biodiesel, this stream is washed with hot water to extract the excess of NaOH or KOH and the soap that could have been formed during the reaction. Glycerol-enriched phase is directed to another flash unit where part of ethanol is recovered. If high purity glycerol is to be obtained, a distillation column working under vacuum conditions (0.2 atm) is required (Gutiérrez et al., 2009).

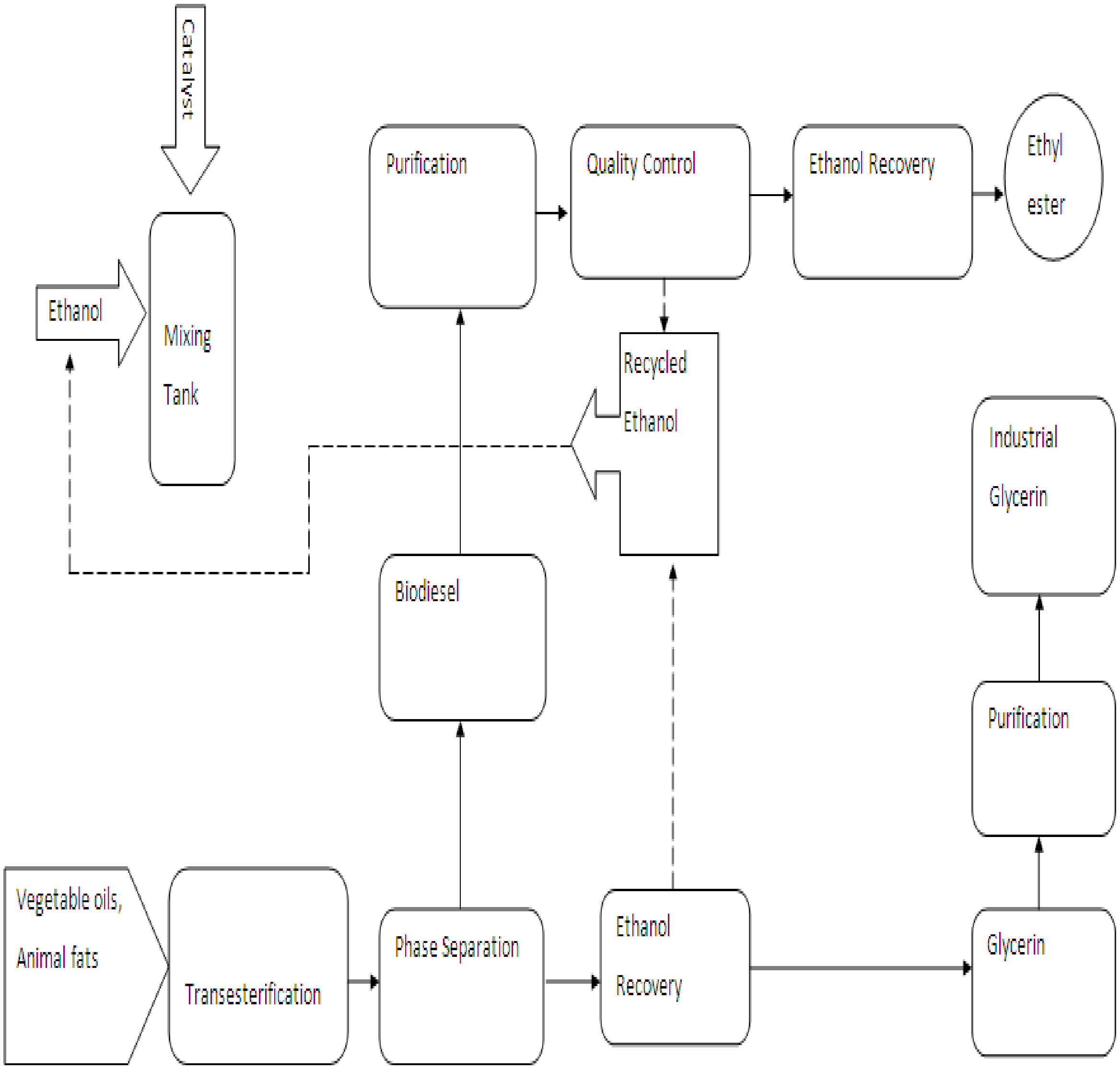


Figure 2.1: Main Step of Biodiesel Production

CHAPTER 3

METHODOLOGY

3.1 Introduction

In order to produce biodiesel, five major steps involved. These steps the equipment selection, raw material preparation, experimental procedure, sample preparation for GC analysis and analytical method. In the experimental at procedure, the reaction was conducted using heterogeneous catalyst, potassium hydroxide (KOH). In this experiment, the molar ratio of ethanol to palm oil was fixed at 6:1 ratios and the reaction temperature at 60°C. To analyze the biodiesel product, gas chromatography was used. The flow process of the experiment was illustrated and discuss in the subtopics below. The general flow of the experiment was illustrated in the figure below.

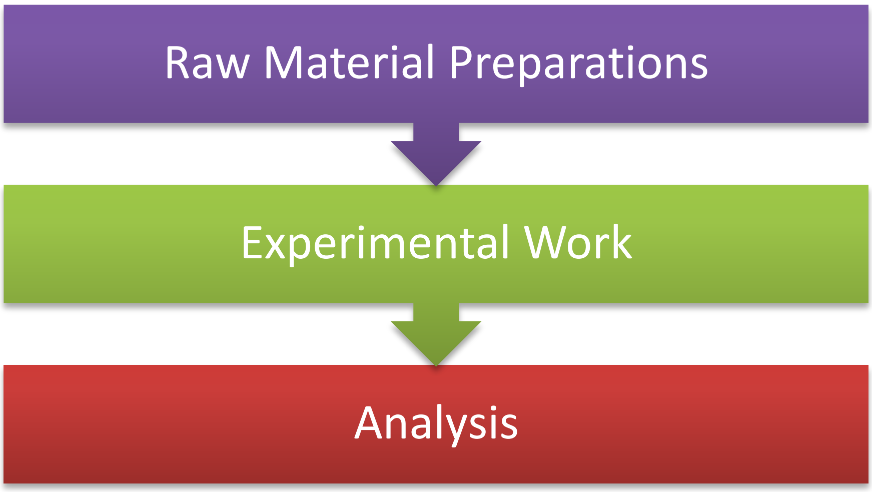


Figure 3.1: Main Methodology Flow Chart

3.2 Equipment Selection

The equipment selection needs to be considered. It will depend on equipment availability in UMP (Universiti Malaysia Pahang) chemical engineering lab and appropriateness of the equipment to the task. The list of equipment and apparatus are shown in **Table 3.2:**

Table 3.1: List of equipment and apparatus

No.	**Equipment/Apparatus**	**Function**
1	2 neck conical flask	The reaction was carried out in the flask
2	Magnetic stirrer bar	Mixing the reactants
3	Condenser	Condensed the sample from being release to the atmosphere
3	Water Bath	Regulating the temperature of substances subjected to heat
5	Gas chromatography	Analyze the composition of product

3.3 Experimental Materials

The raw material palm oil was obtained from a local store and the other chemical was purchased by supplier. List of raw material and chemical substance are show in **Table 3.3**.

Table 3.2: List of chemicals used and its application

Chemicals	**Application**	**Purity/Grade**
Ethanol	Reactant	95%
Potassium hydroxide	Catalyst	100%
Cooking Oil	Reactant	Sri Murni cooking oil
n-heptane	Solvent for oil analysis on GC	HPLC Grade

3.4 Experimental Procedure

3.4.1 Control Experiment

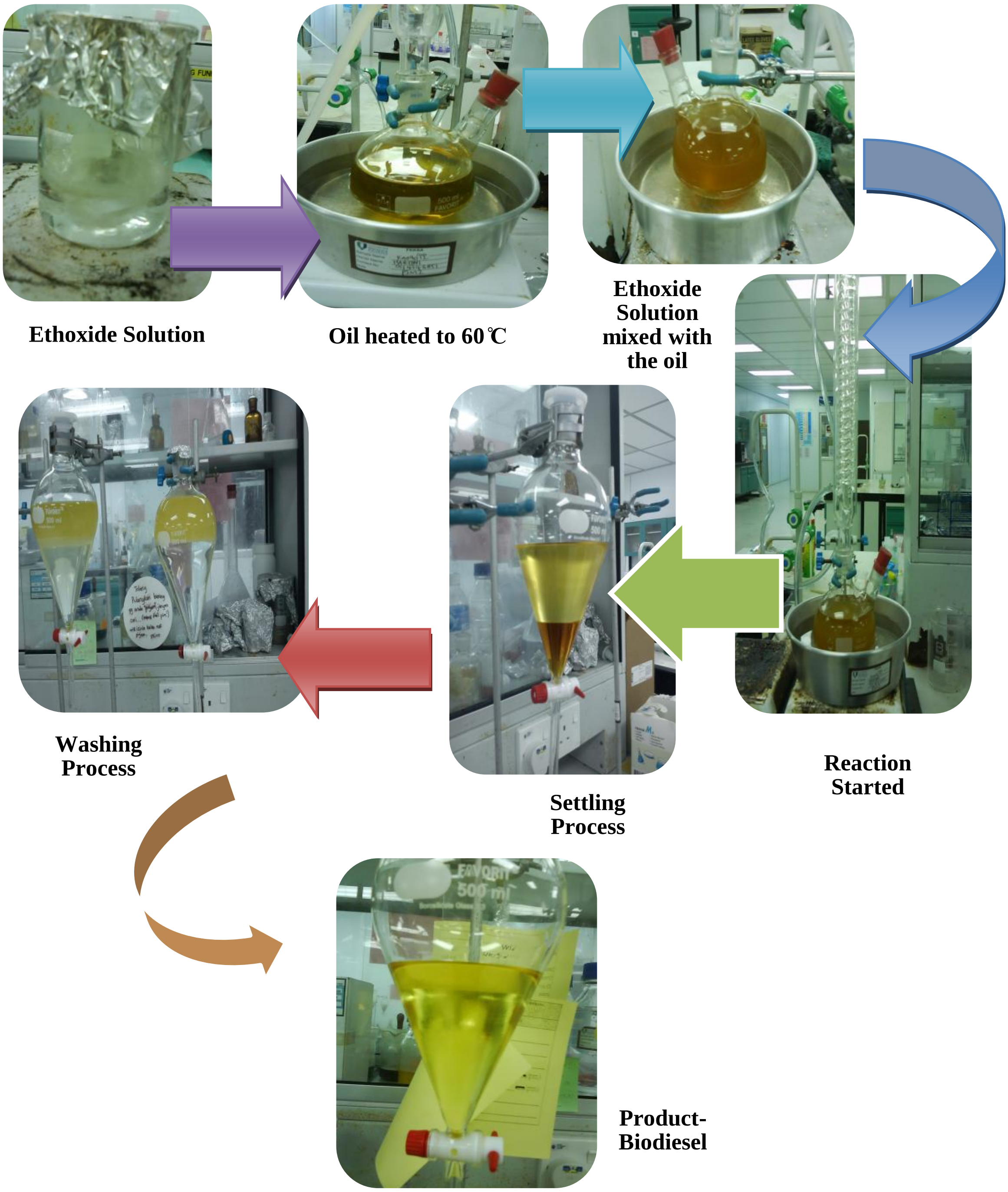


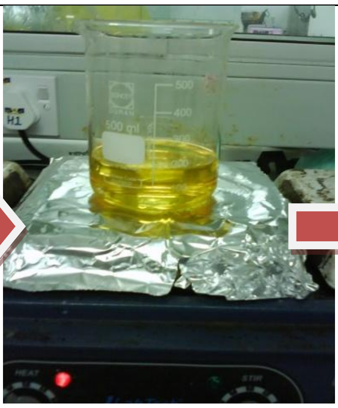
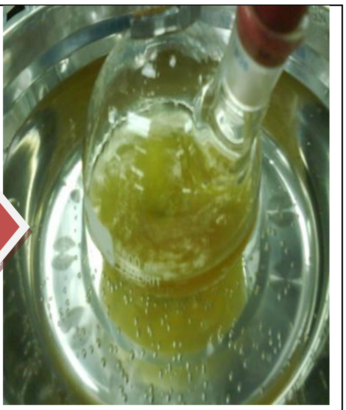
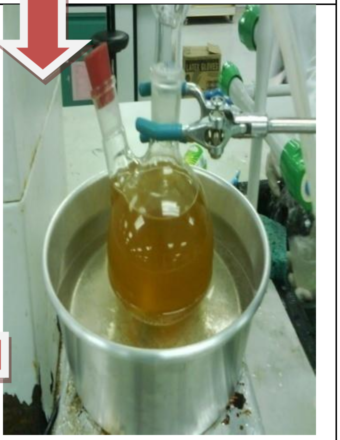
Figure 3.4.1: Process Flow of Control Experimental Work

Firstly, 0.65 g of pallets of potassium hydroxide (KOH) was added into 67 mL of pure (95% purity) ethanol in a 200 mL beaker containing a magnetic stirrer bar. The beaker was then put on a magnetic stirrer plate, and it was stir vigorously until all of the KOH is dissolved. That beaker then contains sodium ethoxide. After that, 183 mL of pure vegetable oil (palm oil) was warm to 60°C in a 500 mL 2-neck round bottom flask. Warming the oil up is not necessary, but it increases the reaction rate. When all of the KOH was dissolved, the 67 mL of the ethoxide solution was pour into the oil while continually stirring. At first the mixture become cloudy, but then separate into three layers. Then, the solution was stir for 1 hour on a fixed temperature of 60℃.

After the reaction stopped, the mixture allowed standing for phase separation. The contents of the flask was then transfer into a 500 mL separatory funnel. The solution was leave to separate for overnight of 15 hour. The mixture was then separate into two different layers. The glycerol fall to the bottom and the ethyl ester (biodiesel) was float to the top. Then open the stopcock of the separatory funnel and the glycerol was allowed to drain into a small beaker.

The biodiesel was then undergoes a washing process to remove impurities from ester. At first 200-250 mL warm tap water was added to the separatory funnel with the biodiesel. The water was then let to settle out of the biodiesel layer, the layer of water was appear on bottom of the funnel and then it was drain out from the funnel. The washing process was repeated up to 3 times. Then, the washed biodiesel was transfer to a beaker. After that, the washed biodiesel was heated to 105^0C in order to boil off all the water that may be remaining.

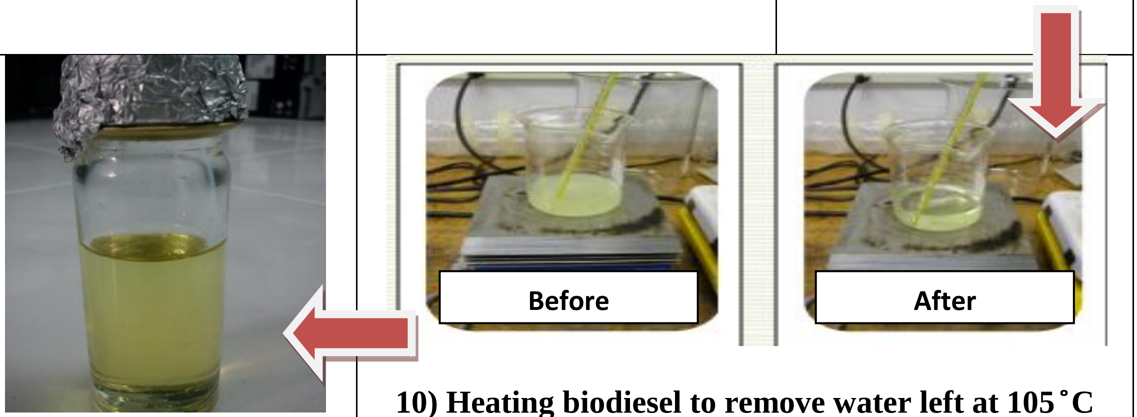
3.4.2 Extractive Reaction Experiment

 1) **Ethoxide Solution**	 2) **Oil heated to 60°C**	 3) **Oil mixed with the ethoxide solution. The reaction started**
 **6) The reaction started back**	 **5) Extract Process**	 4) **The reaction stopped and let to settle**

7) Settling Process

8) Washing Process

9) Biodiesel



10) Heating biodiesel to remove water left at 105˚C

11) Final product

Figure 3.4.2: Process Flow of Extractive Reaction Experiment

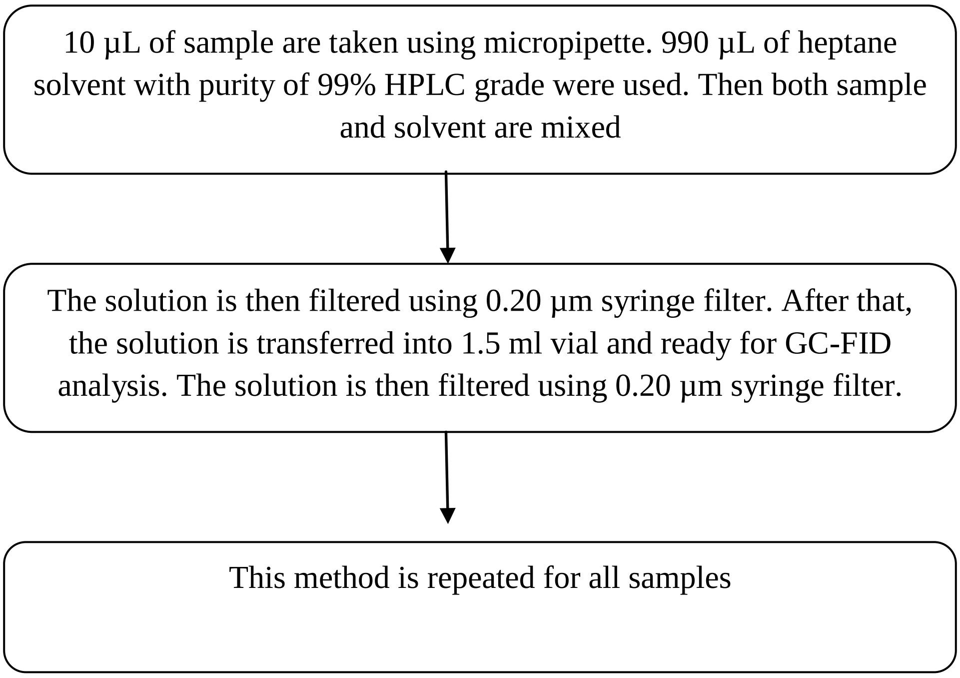
Firstly, 0.65 g of pallets of potassium hydroxide (KOH) was added into 67 mL of pure (95% purity) ethanol in a 200 mL beaker containing a magnetic stirrer bar. The beaker was then put on a magnetic stirrer plate, and it was stir vigorously until all of the KOH is dissolved. That beaker then contains sodium ethoxide. After that, 183 mL of pure vegetable oil (palm oil) was warm to 60°C in a 500 mL 2-neck round bottom flask. When all of the KOH was dissolved, the 67 mL of the ethoxide solution was pour into the oil while continually stirring. The temperature of the reaction process is 60℃.

After 15 minutes the reaction started, the reaction was stopped. The solution was then leave to settle for 30 minutes, three different layers was then appear which is at the top is biodiesel with ethanol, middle layers is oil and bottom layers containing glycerol, water and ethanol. By using micro-pipette (1-10 mL), 10mL of ethanol from the upper layer of the solution was pipette out from the solution. Then, 10mL of pure ethanol was pipette in the solution (this is the first extract). After that, the reaction was started back for 15 minute, and then the reaction was stopped. The solution was then leaving to settle for 30 minutes. Using micro-pipette (1-10 mL), 10mL of ethanol from the upper layer of the solution was pipette out from the solution. Then, 10mL of pure ethanol was pipette in the solution (this is the second extract).

The reaction was started back for 30 minutes and then the reaction stopped. The same procedure as control experiment of settling process and washing process was done to the biodiesel product. This extractive reaction experiment was repeated for 2 more run with 3 and 4 times extract respectively.

3.4.3 Sample Preparation for GC Analysis

Dilution method for sample GC analysis (1% sample)



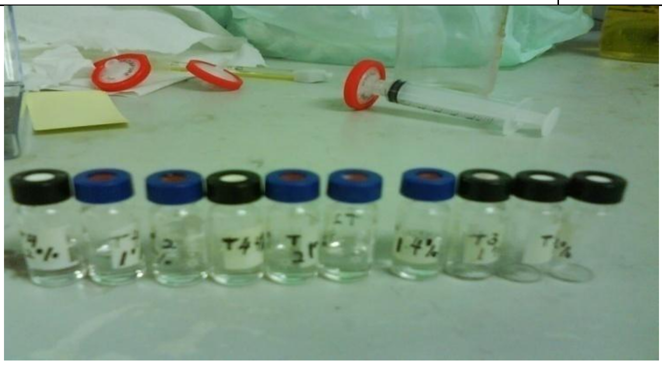
10 µL of sample are taken using micropipette. 990 µL of heptane solvent with purity of 99% HPLC grade were used. Then both sample and solvent are mixed

The solution is then filtered using 0.20 µm syringe filter. After that, the solution is transferred into 1.5 ml vial and ready for GC-FID analysis. The solution is then filtered using 0.20 µm syringe filter.

This method is repeated for all samples

1) Biodiesel diluted with heptane

2) After mixed,filtered to vial



3) Sample ready to analysis using GC-FID

Figure 3.4.3: Sample preparation for analyze using GC-FID

3.5 Analysis

The composition of fatty acid ethyl esters (FAEE) or biodiesel in the upper layer of the reactive extraction products and FAEE product from control experiment were analyzed through Gas Chromatography-Flame Ionized Detector (GC-FID) Analysis Equipment.

3.5.1 Gas Chromatography (GC-FID) Analysis

Gas chromatography is a chemical analysis instrument that for separate chemical in a complex sample. The GC instruments vaporize the sample and then separate and analyze the various components. Each component ideally produces a specific spectral peak that may be recorded on a computer that connects with the instrument. The time elapsed between injection and elution is called the “retention time”. The retention time is taking is less than 180 seconds that can help to differentiate between some compounds. The size of the peak is proportional to the quality of the corresponding substances in the specimen analyzed. The peak is measured from the baseline to the tip of the peak. The carrier gas use in the analysis is hydrogen. The flame ionization detector (FID) is a non-selective detector used in conjunction with gas chromatography. Because it is non-selective, there is a potential for many non-target compounds present in samples to interfere with this analysis and for poor resolution especially in complex samples. The FID works by directing the gas phase output from the column into a hydrogen flame. A voltage of 100-200V is applied between the flame and an electrode located away from the flame. The increased current due to electrons emitted by burning carbon particles is then measured. Although the signal current is very small (the ionization efficiency is only 0.0015%) the noise level is also very small (<10-13 amp) and with a well-optimized system, sensitivities of 5 x 10-12 g/ml for n-heptane at a signal/noise ratio of 2 can be easily realized. Except for a very few organic compounds (e.g. carbon monoxide, etc.) the FID detects all carbon containing compounds.

Table 3.5: Gas Chromatography Flame Ionization Detector (FID)

Temperature column	Initially held at 220°C for 4 min, then ramped to 230 °C with 10^0C/min (held for 3 min), and finally ramped up at 10^0C/min to 250 °C and maintained for 20 min.
Injector and Detector temperature	250^0C
Injection size	1.0μL (10:1 split)
Hydrogen flow	35mL/min
Air flow	450mL/min
Nitrogen make up	35mL/min
Carrier gas	Hydrogen, compressed air, H2, N2
Type of Column	DB-WAX 122-7032

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The results are divided into 3 parts, which are results based on control experiment, extractive reaction experiment and normalized peak area result. In this thesis all the result are discussed in order to find out either the extractive reaction of biodiesel synthesis using ethanol as a solvent has improved the extraction rate or not.

4.2 Control Experiment

In this experiment, the conventional biodiesel production was run. The FAEE (biodiesel) product from this control experiment will be the control one to compare with the product from the extractive reaction experiment. The temperature and reaction time was fixed at 60˚C and 1 hour respectively. The molar ratio ethanol to palm oil was 6:1 and total volume of solution also fixed at 250 mL.

Table 4.2 shows the results obtain from the GC analysis. By not doing any extractive reaction this is the peak area obtain. Soon on this chapter I will discuss the comparison of with and without extraction system.

Table 4.1: Peak Area of Control Experiment

Control Number	Peak Area (pA*s)
Control 1	7342.6645
Control 2	7436.7139

4.3 Extractive Reaction Experiment

In this study, the extraction system was applied to the biodiesel production. The temperature, reaction time, molar ratio and total volume of solution were fixed the same as the control experiment in order to make it easier for comparison. The numbers of extracting the fresh ethanol are very vital throughout the experiment. Three run of extractive reaction was done; the result from GC analysis was tabulated in **Table 4.2**. The temperature and reaction time was fixed at 60˚C and 1 hour respectively. The molar ratio ethanol to palm oil was 6:1 and total volume of solution also fixed at 250 mL.

Table 4.2: Peak Area of Extractive Reaction Experiment

Number of Extraction	Peak Area (pA*s)
2	7606.49805
3	6428.21924
4	6021.13135

From the result obtain, the more times of extract the fresh ethanol the lower the peak area obtain. Since the reaction only happens in oil, the extraction system has improved the extraction property of the oil.

4.4 Normalizing Peak Areas Method

Data from chromatograms may be used to obtain the relative concentrations of components in a mixture, providing good resolution is achieved. The peak area, from integration of the detector signal during elution of a component, is proportional to the amount of that component in the sample. However, the response of a detector varies from one compound to another; for example GC flame ionization detector depends on the formation of ions. Thus, a set of detector response factors needs to be determined for a particular analysis. Although many integrators include area % in the printout this is not the true ratio of the components. Area % is simply the area of an individual peak calculated as a percentage of the total areas recorded for all peaks in the chromatogram. It can be useful for a quick check of replicate analyses. One of the principal methods for obtaining quantitative information is normalizing the peak area method.

The area of each peak is obtained from a series of replicate injections of a mixture containing equal (or known) amounts of all the components. Acceptable precision is essential to obtain satisfactory data. One component is chosen as the reference, in this study the pure vegetable oil (palm oil) was chosen as the reference. The relative responses of the other components are determined by dividing the peak areas by that of the reference component. The detector response factors (DRF) may then be used to calculate corrected peak areas (A correct) for other analyses involving these components and hence their percentage ratios in the mixture may be determined.

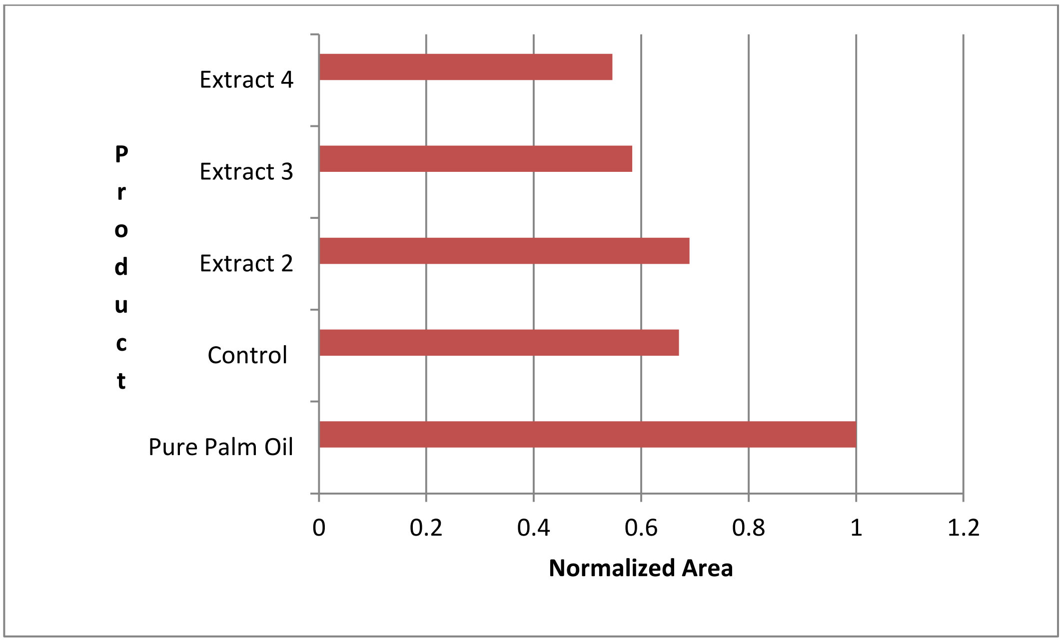


Figure 4.1: Normalized Peak Area

Figure 4.1 shows the overall normalized peak area of the product which is biodiesel from the biodiesel synthesis process. The pure palm oil was also analysis, it use as the reference for triglyceride of this research. The entire graph shows the decreasing of peak area when the number of extract is increasing and it is expected. The peak area that measure in this research is triglyceride peak. Main feedstock for biodiesel production analyzed in this work is palm oil that is a mixture of triglycerides.

The overall process for biodiesel production comprises the following steps: feedstock conditioning, reaction, separation, and product purification. During feedstock conditioning, the content of water and free fatty acids in the vegetable oil was controlled in order to avoid undesirable reactions and products (soap). Thus, the conditioning strongly depends on the extraction method of the vegetable oil and on its origin. The reaction step includes the transesterification reaction between the triglycerides of the oil and low molecular weight alcohols (ethanol) in the presence of a catalyst (KOH) to form fatty esters (biodiesel) and glycerol. The transesterification comprises three successive reversible reactions in which each one of the fatty acids linked to glycerol are to be esterified. The first step is the conversion of the triglycerides into diglycerides followed by the conversion of the diglycerides into monoglycerides and, finally, the conversion of the monoglycerides into glycerol producing one molecule of the ester per each glyceride in each step. The main products are the esters of the fatty acids (biodiesel) and glycerol.

Only the triglyceride peak measure in this study. From the bar chart obtain above we can compare the extraction system with the conventional biodiesel production by it peak area. It proved that by extracting fresh ethanol, the peak area of triglyceride become lower, it mean more oil was extract during the reaction. Thus, the extraction rate was improved during the reaction. Therefore, by increasing the number of extract in the reaction mixture, more oil can be extracted out faster and easier and subsequently being transesterified to FAEE.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

By performing the research studies based on the research objectives that have been proposed, the extraction rate on the conversion of ethanol in biodiesel synthesis was determined. From the research studies performed, it shows that the extraction rate become higher when the extractive reaction was applied as it compare to conventional biodiesel production without extractive reaction. As a conclusion, ethanol have a better oil extraction property when applying the extarctive reaction method.

5.2 Recommendation

There are many types of variables affecting the transesterification reaction such as catalyst type and concentration, mixing intensity, effect of reaction time and effect of using organic co solvents. It is recommended that, other parameter should be tested in the transesterification reaction process.

The system that are used in this research studies are batch process. The transesterification process should be done in a continuous reactor to improve the conversion of the ethyl ester. It is also recommended to do the extractive reaction on the reaction rate of ethanol and oil during the reaction process. The extraction rate will be effective by doing the reaction rate study.

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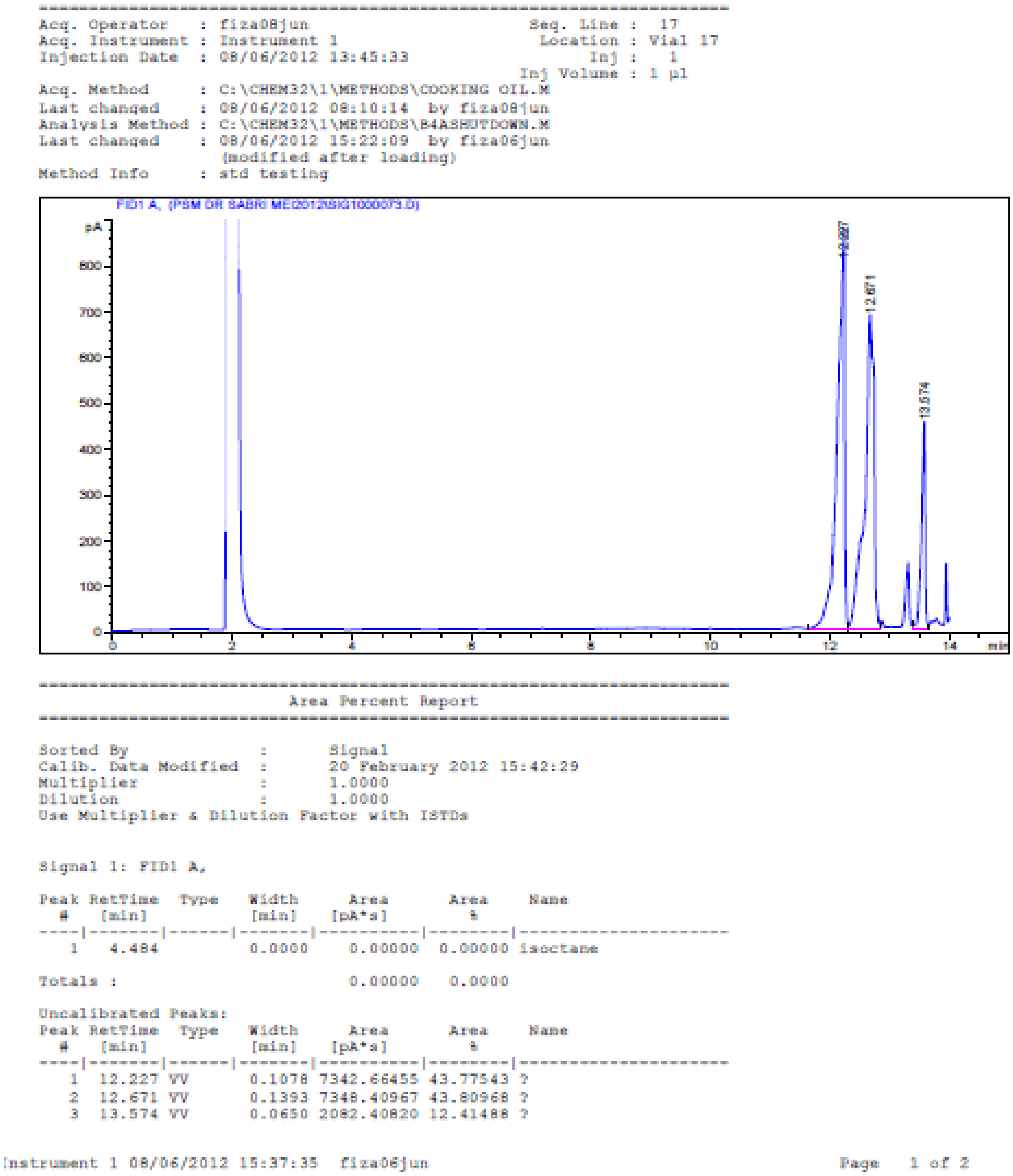
APPENDIX A

DATA FROM GAS CHROMATOGRAPHY ANALYSIS



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Totals :                       0.00000   0.0000

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   3  13.574 VV      0.0650 2082.40820 12.41488 ?

Instrument 1 08/06/2012 15:37:35   fiza06jun                     Page    1 of 2
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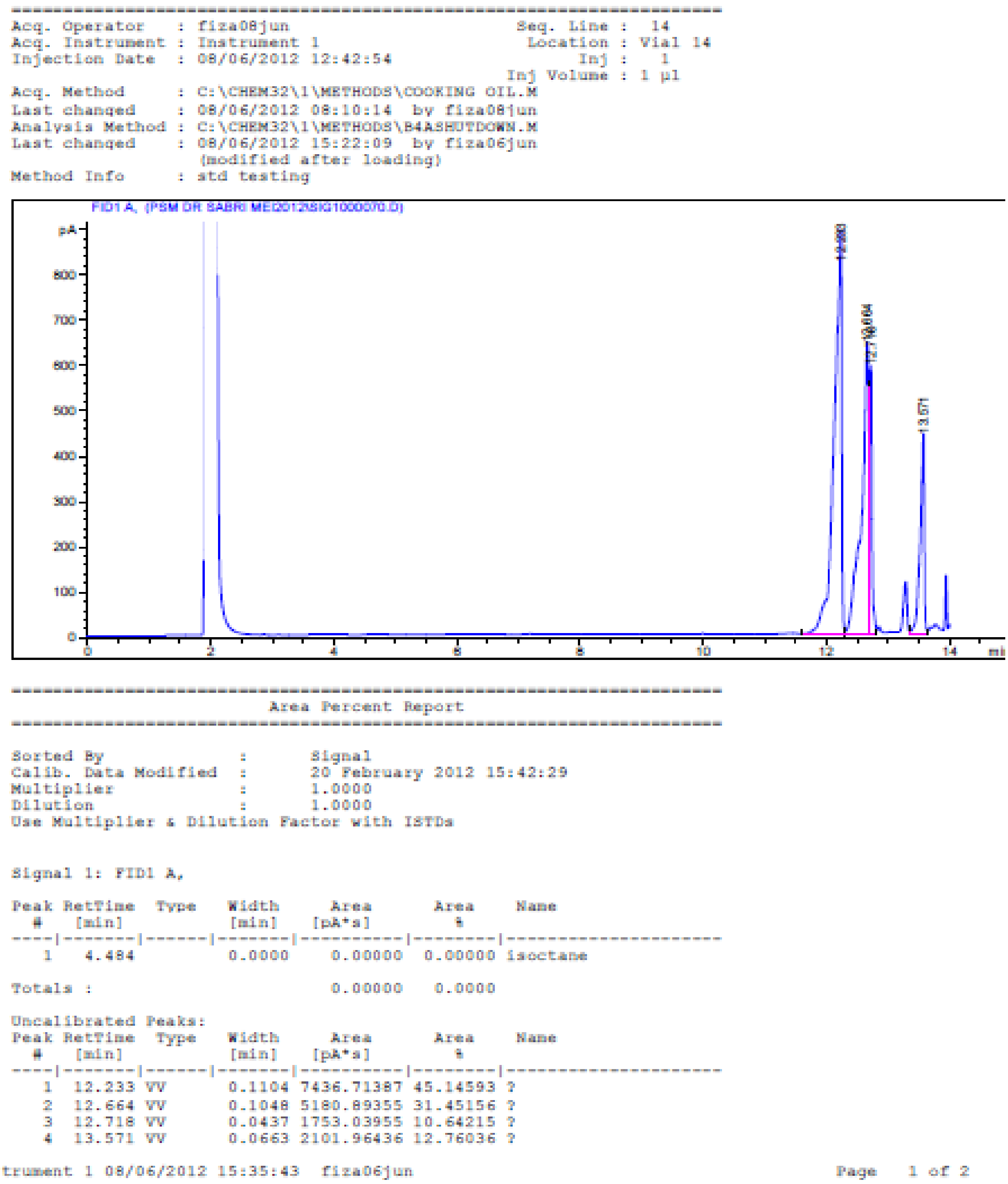
Figure A1: Data for Control Biodiesel 1



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Totals :                      0.00000   0.0000

Uncalibrated Peaks:
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   2  12.664 VV     0.1048 5180.89355 31.45156 ?
   3  12.718 VV     0.0437 1753.03955 10.64215 ?
   4  13.571 VV     0.0663 2101.96436 12.76036 ?
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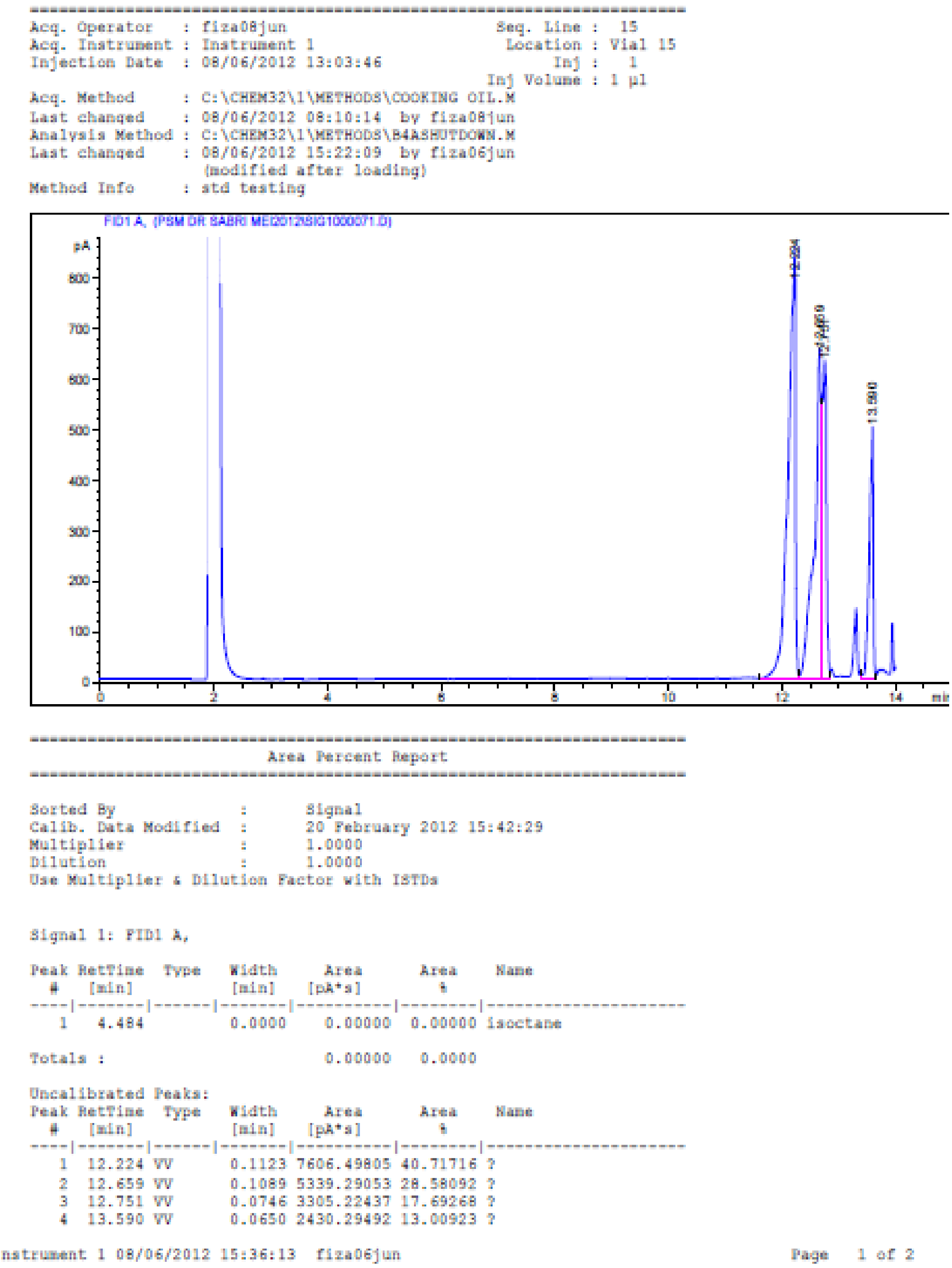
Figure A2: Data for Control Biodiesel 2



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Method Info     : std testing
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Use Multiplier & Dilution Factor with ISTDs


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Totals :                        0.00000   0.0000

Uncalibrated Peaks:
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   3  12.751 VV      0.0746 3305.22437 17.69268 ?
   4  13.590 VV      0.0650 2430.29492 13.00923 ?
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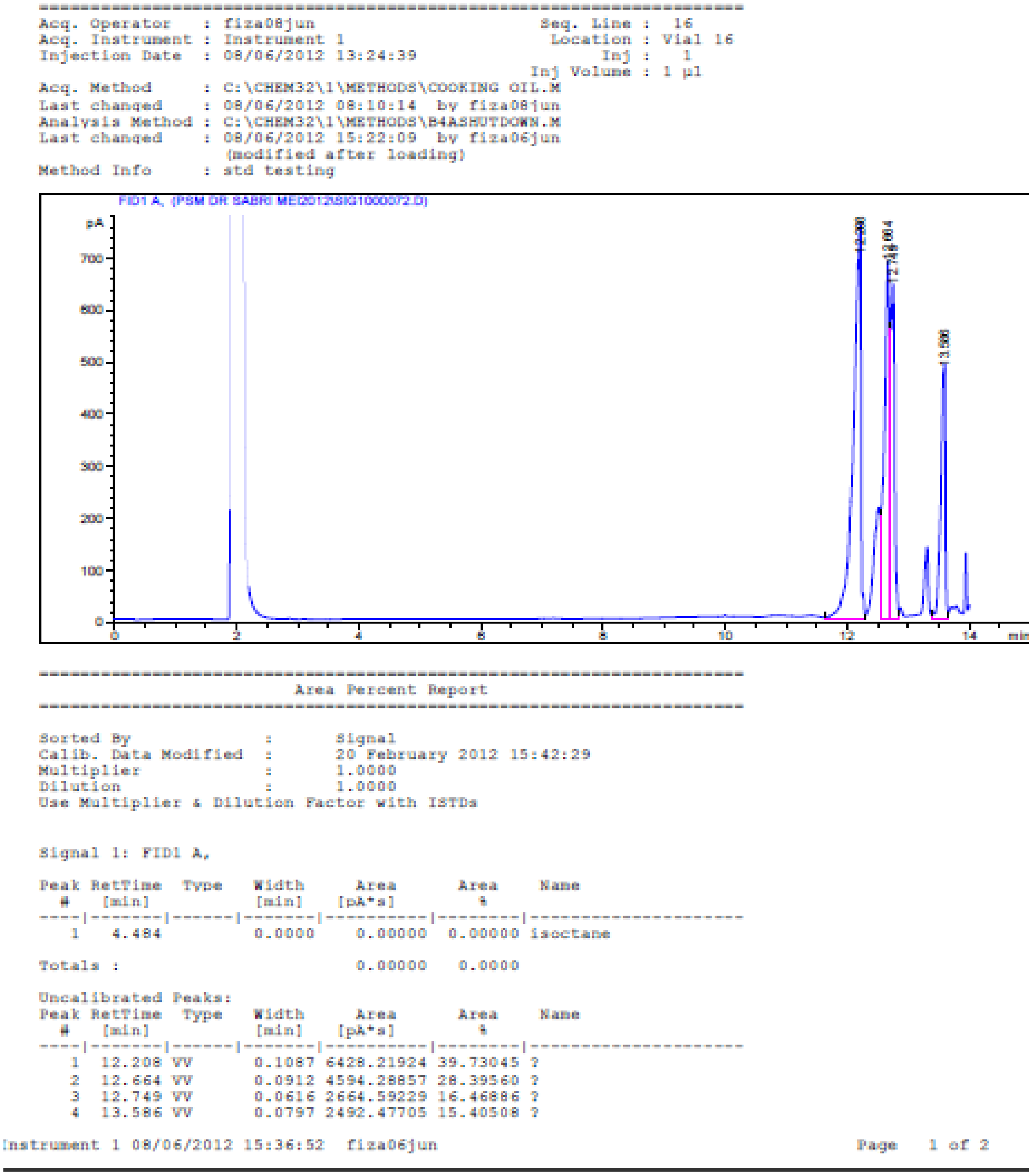
Figure A3: Data for Extract 2



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Use Multiplier & Dilution Factor with ISTDs


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   1   4.484         0.0000     0.00000  0.00000 isoctane

Totals :                        0.00000   0.0000

Uncalibrated Peaks:
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   4  13.586 VV      0.0797 2492.47705 15.40508 ?

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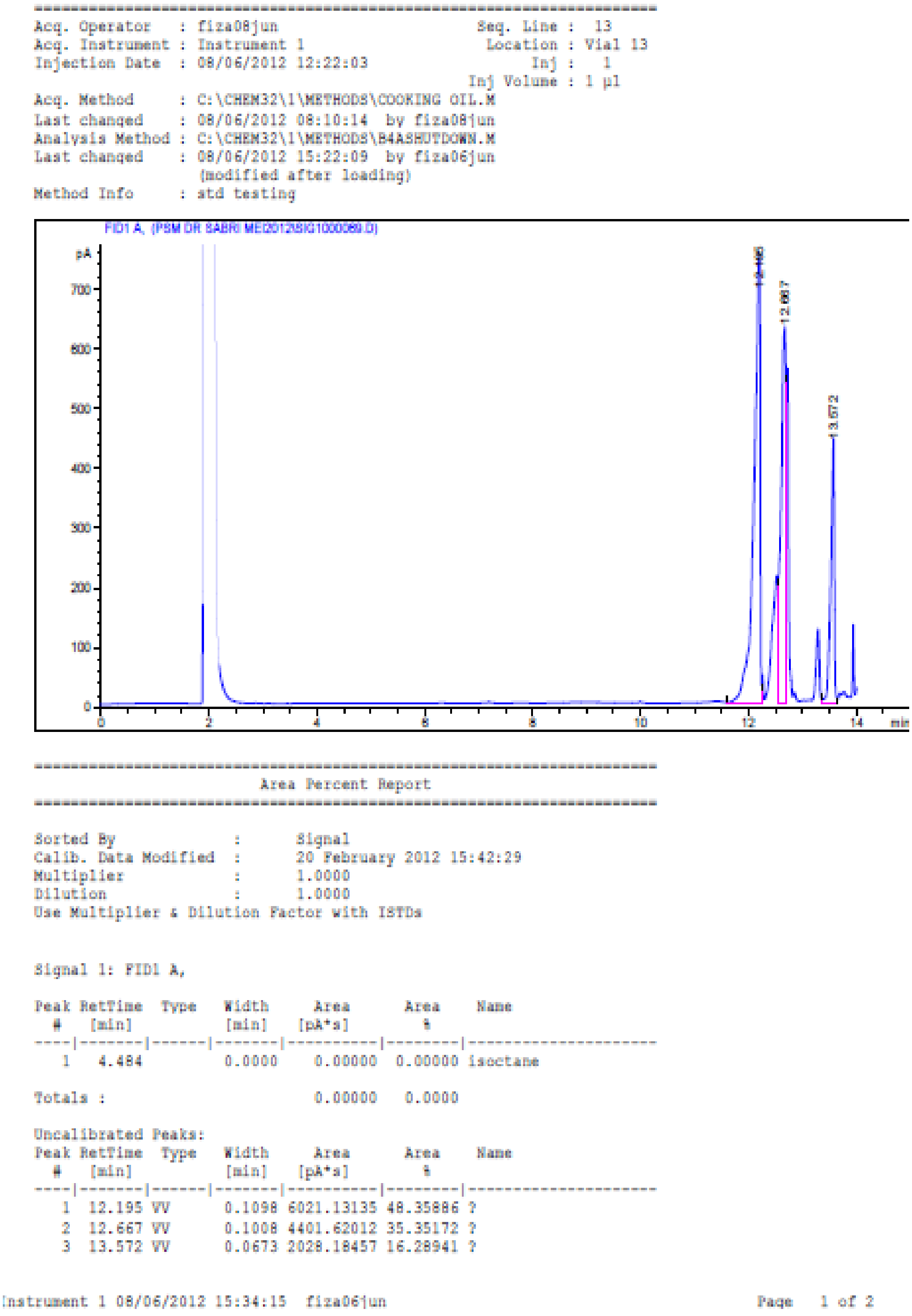
Figure A4: Data for Extract 3



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Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
Last changed    : 08/06/2012 15:22:09  by fiza06jun
                  (modified after loading)
Method Info     : std testing
```

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

Sorted By             :      Signal
Calib. Data Modified  :      20 February 2012 15:42:29
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

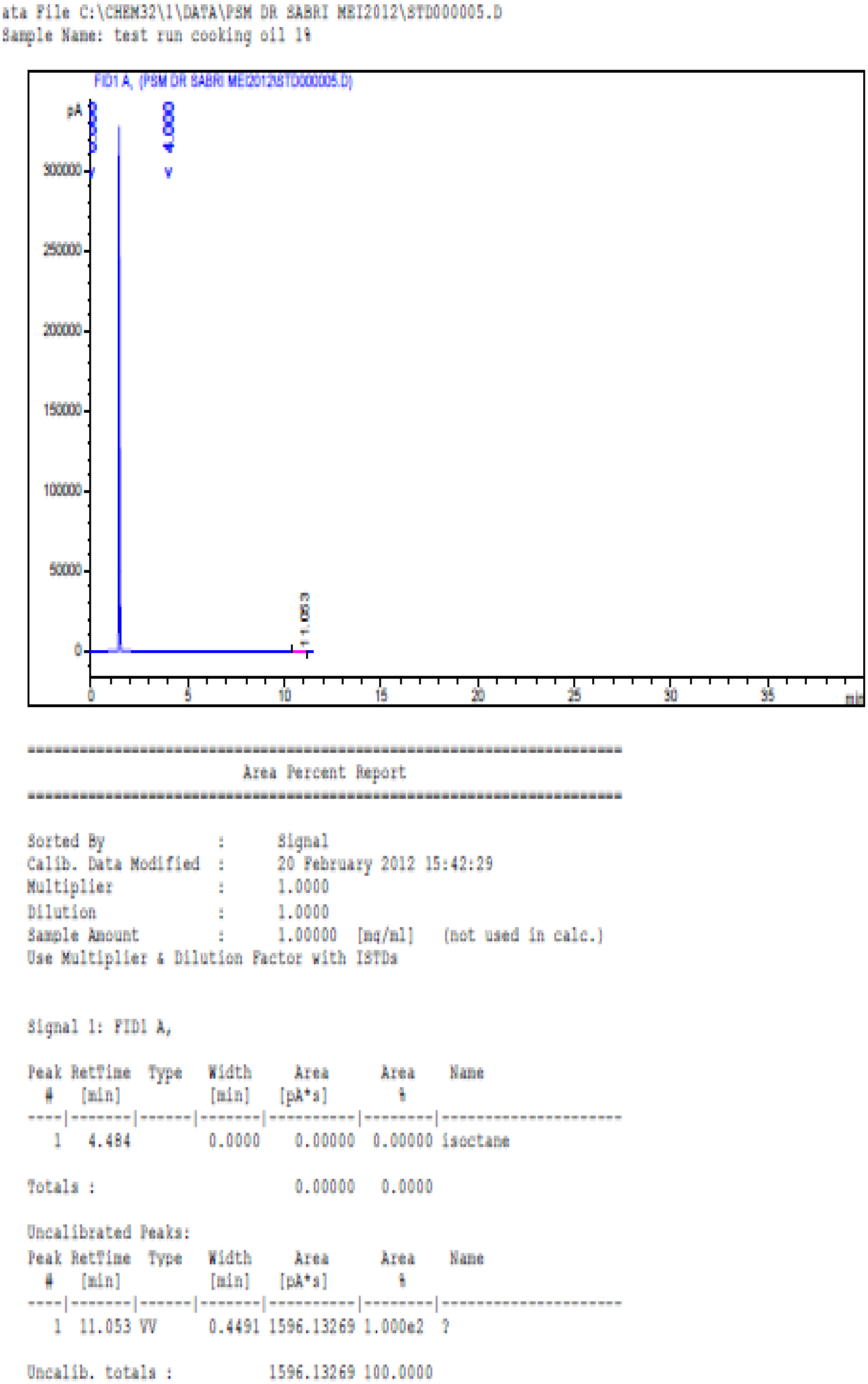
Peak RetTime  Type  Width     Area      Area    Name
  #   [min]         [min]    [pA*s]      %
----|-------|------|-------|----------|--------|---------------------
   1   4.484         0.0000    0.00000  0.00000 isoctane

Totals :                       0.00000   0.0000

Uncalibrated Peaks:
Peak RetTime  Type  Width     Area      Area    Name
  #   [min]         [min]    [pA*s]      %
----|-------|------|-------|----------|--------|---------------------
   1  12.195 VV      0.1098 6021.13135 48.35886 ?
   2  12.667 VV      0.1008 4401.62012 35.35172 ?
   3  13.572 VV      0.0673 2028.18457 16.28941 ?

Instrument 1 08/06/2012 15:34:15  fiza06jun                  Page   1 of 2
```

Figure A5: Data for Extract 4



```
ata File C:\CHEM32\1\DATA\PSM DR SABRI MEI2012\STD000005.D
Sample Name: test run cooking oil 1%
```

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

Sorted By             :      Signal
Calib. Data Modified  :      20 February 2012 15:42:29
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [mg/ml]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime  Type   Width     Area      Area    Name
  #   [min]          [min]    [pA*s]       %
----|-------|------|-------|----------|--------|---------------------
   1   4.484         0.0000    0.00000  0.00000 isoctane

Totals :                       0.00000   0.0000

Uncalibrated Peaks:
Peak RetTime  Type   Width     Area      Area    Name
  #   [min]          [min]    [pA*s]       %
----|-------|------|-------|----------|--------|---------------------
   1  11.053 VV      0.4491 1596.13269 1.000e2  ?

Uncalib. totals :           1596.13269 100.0000
```

Figure A6: Data for Pure Palm Oil