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PURIFICATION OF BIODIESEL USING ADSORBENTS AND SATURATED SALT SOLUTION

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งานวิจัยนี้ศึกษาการทำไบโอดีเซลให้บริสุทธิ์โดยใช้ตัวดูดซับและสารละลายเกลืออิ่มตัว ไบโอดีเซลสังเคราะห์จากกระบวนการทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มกับเมทานอล โดยใช้อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเท่ากับ 6:1 โซเดียมไฮดรอกไซด์ร้อยละ 1 ของน้ำหนักน้ำมัน อุณหภูมิ 60 องศาเซลเซียส เวลา 1.50 ชั่วโมง ทำการล้างไบโอดีเซลด้วยสารละลายเกลืออิ่มตัว 3 ชนิด ได้แก่ โซเดียมคลอไรด์ โพแทสเซียมคลอไรด์ และเฟอร์ริกซัลเฟต พบว่าสารละลายเกลืออิ่มตัวของโซเดียมคลอไรด์ให้ผลการทดลองที่ดีที่สุดในการกำจัดสบู่ โดยภาวะที่เหมาะสมคืออัตราส่วนระหว่างไบโอดีเซลต่อสารละลายเกลืออิ่มตัวของโซเดียมคลอไรด์เท่ากับ 1:1 ทำการล้าง 1 ครั้งโดยใช้เวลา 30 วินาที ที่อุณหภูมิห้อง ไบโอดีเซลที่ทำการล้างด้วยสารละลายเกลืออิ่มตัวของโซเดียมคลอไรด์สามารถลดปริมาณสบู่จาก 3500 ppm เหลือ 28 ppm จากนั้นนำไบโอดีเซลมาทำให้บริสุทธิ์เพิ่มเติมโดยใช้ตัวดูดซับ ได้แก่ ซิลิกาเจล ถ่านกัมมันต์ และดินกัมมันต์ กระบวนการนี้ให้คุณภาพของไบโอดีเซลเทียบเท่ากับกระบวนการล้างด้วยน้ำ และให้ค่าความเป็นกรด ความหนืด จุดวาบไฟ และกลีเซอรีนอิสระและกลีเซอรีนทั้งหมดผ่านเกณฑ์มาตรฐานของไบโอดีเซล

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This research studied the purification of biodiesel using adsorbents and saturated salt solution. The biodiesel was synthesized by the transesterification of palm oil with methanol at 6:1 molar ratio of methanol:oil, 1 %wt of sodium hydroxide and reaction temperature of 60°C for 1.50 hours. The crude biodiesel was subjected to wash with three types of saturated salt solution including sodium chloride, potassium chloride and ferric sulfate. It was found that the saturated salt solution of sodium chloride gave the best result for removal of soap and the optimum conditions were 1:1 ratio of crude biodiesel and saturated salt solution of sodium chloride, one time of washing for 30 seconds at room temperature. By washing crude biodiesel with saturated salt solution of sodium chloride, the soap content could be reduced from 3500 ppm to 28 ppm. Then, the biodiesel was further purified by using adsorbents including silica gel, activated carbon and activated clay. This process gave the quality of biodiesel as analogous to water washing process and values of acid number, viscosity, flash point and free and total glycerin passed the specification of biodiesel standard.

Field of Study : ..Petrochemistry and Polymer Science.Student's Signature……..…...
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CONTENTS

PAGE

ABSTRACT (THAI) iv
ABSTRACT (ENGLISH) v
ACKNOWLEDGEMENTS vi
CONTENTS vii
LIST OF TABLES x
LIST OF FIGURES xii
LIST OF ABBREVIATIONS xiv

CHAPTER I INTRODUCTION 1

1.1 Objectives of the research 2

CHAPTER II THEORY AND LITERATURE REVIEWS 3

2.1 Alternative renewable energy 3
2.2 Production of biodiesel 4
2.2.1 Direct use and blending 4
2.2.2 Micro-emulsions 4
2.2.3 Thermal cracking 5
2.2.4 Transesterification 5
2.3 Transesterification of vegetable oils 6
2.3.1 Effect of reaction parameter 7
2.3.2 Type of catalyst 9
2.4 Biodiesel quality 12
2.5 Solvent extraction 17
2.6 Adsorption 17
2.6.1 Physisorption 18
2.6.1 Chemisorption 18

PAGE

2.7 Adsorbents 18
2.7.1 Silica gel 19
2.7.2 Activated carbon 20
2.7.3 Clay minerals 20
2.8 Literature review 22

CHAPTER III EXPERIMENTAL 24

3.1 Materials and equipments 24
3.1.1 Chemicals and materials 24
3.1.2 Equipments 24
3.2 Procedure 25
3.2.1 Preparation of the saturated salt solutions 25
3.2.2 Synthesis of biodiesel 25
3.2.3 Purification of crude biodiesel by using the saturated salt solutions 25
3.2.3.1 Type of saturated salt solution 25
3.2.3.2 Shaking time 25
3.2.3.3 Ratio between biodiesel and saturated salt solution 26
3.2.3.4 Temperature of washing 26
3.2.3.5 Methanol content in crude biodiesel 26
3.2.4 Purification of crude biodiesel by using adsorbents 26
3.2.5 Purification of crude biodiesel by using water washing 27
3.2.6 Biodiesel analysis 27
3.2.6.1 Determination of the soap content 27
3.2.6.2 Determination of free and total glycerin 28
3.2.6.3 Determination of sodium content 28
3.2.6.3 Determination of the properties of biodiesel 28

PAGE

CHAPTER IV RESULTS AND DISCUSSIONS 30

4.1 Purification of crude biodiesel by using the saturated salt solutions 30

4.1.1 Effect of type of saturated salt solution 30

4.1.2 Effect of the shaking time 31

4.1.3 Effect of the ratio between biodiesel and saturated salt solution 32

4.1.4 Effect of temperature of washing 32

4.1.5 Effect of methanol content in crude biodiesel 33

4.2 Purification of crude biodiesel by using adsorbents compared with water washing 34

4.2.1 Determination of the soap content 34

4.2.2 Determination of free and total glycerin 35

4.2.3 Determination of sodium content 36

4.3 Properties of biodiesel 36

CHAPTER V CONCLUSIONS AND DISCUSSIONS 38

5.1 Conclusion 38

5.2 Suggestion 39

REFERENCES 40

APPENDICES 44

Appendix A 45

Appendix B 67

VITA 87

LIST OF TABLES

TABLE **PAGE**

2.1 Comparison of the different technologies to produce biodiesel 12
2.2 Comparison of fuel properties between diesel and biodiesel 13
2.3 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand 14
3.1 Test method of biodiesel fuels 29
4.1 Soap content and acid value of biodiesel washed with three types of saturated salt solution 30
4.2 Soap content of biodiesel after removed methanol and washed with saturated salt solution (NaCl) for 30 seconds at room temperature 34
4.3 Soap content of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing 34
4.4 Free and total glycerin contents (%wt) of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing 35
4.5 Sodium contents of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing. 36
4.6 Properties of biodiesel 37
B1 Soap content of biodiesel washed with three types of saturated salt solution 67
B2 Soap content of biodiesel washed with saturated salt solution (NaCl) at various shaking time 68
B3 Soap content of biodiesel washed with various ratios of saturated salt solution (NaCl) 69
B4 Soap content of biodiesel washed with saturated salt solution (NaCl) at various temperatures 70
B5 Soap content of biodiesel washed with saturated salt solution (NaCl) after removed methanol 71
B6 Soap content of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing 72

TABLE **PAGE**

B7 Calculation of glycerol calibration function 73
B8 Calculation of glycerol calibration function (continued) 73
B9 Calculation of monoglyceride calibration function 75
B10 Calculation of monoglyceride calibration function (continued) 75
B11 Calculation of diglyceride calibration function 76
B12 Calculation of diglyceride calibration function (continued) 76
B13 Calculation of triglyceride calibration function 77
B14 Calculation of triglyceride calibration function (continue) 77
B15 The percentage of free glycerol (%wt) of biodiesel 79
B16 The percentage of monoglyceride (%wt) of biodiesel 80
B17 The percentage of diglyceride (%wt) of biodiesel 80
B18 The percentage of triglyceride (%wt) of biodiesel 81
B19 The percentage of total glycerin (%wt) of biodiesel 81
B20 Acid value of biodiesel 84
B21 Viscosity of biodiesel 85

LIST OF FIGURES

FIGURE **PAGE**

2.1 General equation for transesterification reaction 6
2.2 Transesterification of vegetable oils 6
2.3 The reaction of sodium methoxide 10
2.4 The reaction of sodium soap 10
2.5 Samples of non-ionic base-catalysts 11
4.1 Effect of the shaking time on soap content in biodiesel using 1:1 ratio of biodiesel and saturated salt solution (NaCl) at room temperature 31
4.2 Effect of the ratio between biodiesel and saturated salt solution (NaCl) on soap content using 30 seconds of the shaking time at room temperature 32
4.3 Effect of temperature of washing on soap content compared with water washing using 1:1 ratio of biodiesel and saturated salt solution (NaCl) and 30 seconds of the shaking time 33
A1 GC chromatogram of EN 14105 standard solution 1 (1) 45
A2 GC chromatogram of EN 14105 standard solution 1 (2) 46
A3 GC chromatogram of EN 14105 standard solution 2 (1) 47
A4 GC chromatogram of EN 14105 standard solution 2 (2) 48
A5 GC chromatogram of EN 14105 standard solution 3 (1) 49
A6 GC chromatogram of EN 14105 standard solution 3 (2) 50
A7 GC chromatogram of EN 14105 standard solution 4 (1) 51
A8 GC chromatogram of EN 14105 standard solution 4 (2) 52
A9 GC chromatogram of unwashed biodiesel (1) 53
A10 GC chromatogram of unwashed biodiesel (2) 54
A11 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) (1) 55
A12 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) (2) 56
A13 GC chromatogram of biodiesel treated with 0.1 % (w/w) silica gel (1) 57
A14 GC chromatogram of biodiesel treated with 0.1 % (w/w) silica gel (2) 58
A15 GC chromatogram of biodiesel treated with 0.1 % (w/w) activated carbon (1) 59
A16 GC chromatogram of biodiesel treated with 0.1 % (w/w) activated carbon (2) 60
A17 GC chromatogram of biodiesel treated with 0.1 % (w/w) activated clay (1) 61

FIGURE **PAGE**

A18 GC chromatogram of biodiesel treated with 0.1 % (w/w) activated clay (2) 62
A19 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) and water (1) 63
A20 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) and water (2) 64
A21 GC chromatogram of biodiesel washed with water 65
A22 GC chromatogram of fatty acid composition 66
B1 The standard curve of sodium standard solution 82

LIST OF ABBREVIATIONS

µl	=	Microliter
µm	=	Micrometer
ASTM	=	American Standard Test Method
°C	=	Degree Celsius
EN	=	European Standards
FFA	=	Free fatty acid
FID	=	Flame Ionization Detector
g	=	Gram
GC	=	Gas-liquid chromatography
h	=	Hour
m	=	Meter
min	=	Minute
mg	=	Milligram
ml	=	Milliter
mm	=	Millimeter
No.	=	Number
ppm	=	Parts per million
rpm	=	Revolution per minute
v/v	=	Volume by volume
w/w	=	Weight by weight
% conversion	=	Percentage conversion
% wt	=	Percentage weight
% yield	=	Percentage yield

CHAPTER I

INTRODUCTION

Nowadays, the consumption of diesel fuel in Thailand is being rather continuously increased. The energy demands and the petroleum crisis have resulted in fuel price, while conventional fuel reserves are limited. Finding a new, renewable and sustainable energy source is necessary for substitution of the petroleum-based fuel. One promising renewable source of energy is biodiesel.

Biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oils or animal fats, which are composed of triglycerides. Since biodiesel has proper viscosity and boiling point, high cetane number and also free of sulfur and aromatics, it is considered as an environmentally friendly and nontoxic fuel [1-2]. The way to produce biodiesel is by the transesterification reaction between triglycerides and alcohol, mostly methanol due to its low cost. Transesterification of vegetable oils to biodiesel can be carried out using either heterogeneous or homogeneous catalysts, especially alkaline hydroxide [3]. After the separation process, the biodiesel contains several impurities such as glycerol, glycerides, soap, free fatty acids, methanol, catalyst, metals and water that must be removed from the product. The common process that widely use to purify biodiesel is water washing. However, the major problems in this process are large amount of wastewater produced from cleaning the products and the remained water-insoluble impurities. Moreover, soap can generate emulsion of water and biodiesel that cause separation problem [4-5].

To solve these problems, the application of adsorbents becomes attractive method of biodiesel purification. There are many adsorbents that use to purify biodiesel such as activated carbon, silica gel, magnesium silicate, clays and alumina [6]. The process using saturated salt solution and absorbents is more advantageous than water washing process because both the water-soluble and water-insoluble impurities are eliminated and this process does not generate wastewater.

Objectives of the research:

The objective of this research is to develop on environmentally friendly process for purifying biodiesel using saturated salt solution and adsorbents.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Alternative renewable energy

While the energy demand is continually increasing, the fossil fuel resources are reduced and finite. Therefore, the alternative renewable energy has become an interest globally as the research has directed toward solar tower, dams and alternative energy. Biofuel with low molecular weight can be used for engine fuel instead of diesel fuel. More than one hundred years ago, when Dr. Rudolf Diesel demonstrated the first diesel engine at the World Exhibition in Paris in 1900, he used 100% peanut oil as fuel and promoted the use of vegetable oil as fuel by suggesting that it would greatly benefit the development of agriculture in countries that utilized this potential [7]. In 1930s and 1940s vegetable oils were used as diesel fuel but usually in emergency situation only. Recently, due to increase of crude oil prices, limited resources of fossil fuel and environmental concerns, there has been focusing on vegetable oils and animal fats to make biodiesel.

Biodiesel is a nonpetroleum-based fuel derived from vegetable oils or animal fats and it is used in diesel engines and heating systems. Biodiesel is monoalkyl esters which formed by transesterification or alcoholysis of the triglyceride from the vegetable oils or animal fats with a low-molecular weight alcohol such as methanol or ethanol. This reaction can be activated in presence of catalyst and without catalyst. Generally, the manufacture uses a strong base such as sodium or potassium hydroxide as catalyst. Biodiesel has great advantages compared with the diesel fuel [8]:

- Biodiesel contributes no sulfur at all to the atmosphere (diesel uses sulfur as a lubricant).
- Biodiesel adds no new carbon dioxide to the atmosphere.
- Biodiesel has cetane ratings slightly higher than diesel.
- Biodiesel is both non-toxic and fully-biodegradable.
- Biodiesel has a higher flash point than diesel and is therefore much safer to store.

- Biodiesel can be made from waste restaurant oils and animal fats.
- Biodiesel can be blended in any proportion with petroleum diesel fuel.

Although biodiesel has several advantages, important operating disadvantages of biodiesel in comparison with diesel fuel are cold start problems, the lower energy content, higher cloud point and pour point, higher copper strip corrosion and fuel pumping difficulty from higher viscosity. Biodiesel also increase nitrogen oxides (NOx) emissions compared with diesel fuel used in an unmodified diesel engine. Moreover, peak torque is less for biodiesel than diesel fuel but occurs at lower engine speed and generally the torque curves are flatter. The biodiesel on the average decreases power by 5% compared to that of diesel at rated load [9-10].

2.2 Production of biodiesel

There are four primary ways to produce biodiesel, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification.

2.2.1 Direct use and blending

There was considerable discussion about using of vegetable oil as a fuel in 1980. Batholomew suggested that petroleum should be the alternative fuel rather than vegetable oil and alcohol being the alternative and some form of renewable energy must begin to replace the nonrenewable resource [11]. Caterpillar Brazil used pre-combustion chamber engines with the mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine [12]. It was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful and some experiments used up to a 1:1 ratio. However, direct use of vegetable oil or blending of the oil has generally been considered to be not satisfactory and impractical for both direct and indirect to oxidation, polymerization during storage and diesel engines. The high viscosity, acid composition, combustion, carbon deposits and lubricating oil free fatty acid content, as well as gum formation due thickening are obvious problems.

2.2.2 Micro-emulsions

Micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been investigated to solve the problem of the high viscosity of vegetable

oils. A micro-emulsion is a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm range, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. The ternary phase equilibrium diagram and the plot of viscosity and solvent fraction were used to determine the emulsified fuel formulations. All microemulsions with butanol, hexanol and octanol met the maximum viscosity requirement for No. 2 diesel. 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil and methanol was often used due to its economic advantage over ethanol [13].

2.2.3 Thermal cracking

Thermal cracking or pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst, involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. Catalytic cracking of vegetable oils to produce biofuels has been studied [14]. Copra oil and palm oil stearin were cracked over a standard petroleum catalyst SiO_2/Al_2O_3 at 450°C to produce gases, liquids and solids with lower molecular weights. The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels. The equipment for thermal cracking is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel**.**

2.2.4 Transesterification

Transesterification or alcoholysis is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Among all these alternatives, the transesterification seems to be the

best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

2.3 Transesterification of vegetable oils

Transesterification is the general term used to describe organic reactions where an ester reacts with alcohol to produce another ester as shown in Figure 2.1.

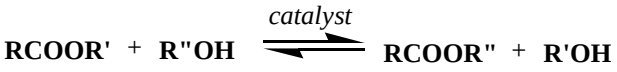

Figure 2.1 General equation for transesterification reaction

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of catalyst to produce a mixture of alkyl esters and glycerol as shown in Figure 2.2 [15].

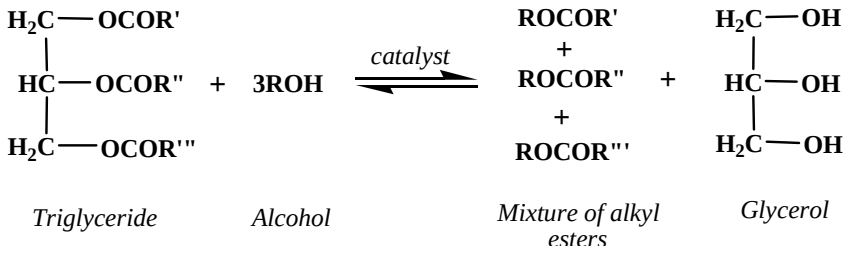

Figure 2.2 Transesterification of vegetable oils

Excess alcohol is used to shift the equilibrium to the product side as the reaction is reversible. There are many types of alcohol that can be used in the transesterification process which short chain such as methanol, ethanol, propanol and butanol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physicals and chemical advantages [3, 12]. Moreover, methanol can quickly react with triglyceride and sodium hydroxide is easily dissolved in it.

2.3.1 Effect of reaction parameter

2.3.1.1 Free fatty acids

Free fatty acids (FFAs) are the saturated or unsaturated monocarboxylic acids in fats, oils or greases but are not attached to glycerol backbones. Higher amount of FFA leads to higher acid value. Vegetable oils should have FFA below a desired level (ranging from less than 0.5% to less than 3%) for base-catalyzed transesterification because the product will change to soap instead of esters. The application of the acid catalyst is to reduce the FFA to the desired limit safe enough for alkali transesterification. Therefore, the transesterification reaction is one-step process for oils with FFA within the range and oils with FFA exceeding the range will use a two-step process, acid esterification is followed by alkali transesterification.

2.3.1.2 Water content

The oils being used as starting material should be free from water content. About 0.1% of water content has been reported to decrease the conversion of ester to a significant extent [16] and also cause soap formation in base-catalyzed process. The moisture can be removed by heating the oil or dissolving the catalyst in methanol before starting the transesterification reaction [17].

2.3.1.3 Molar ratio of alcohol

The molar ratio of alcohol-to-vegetable oil is one of the most important variables that affect the ester yield. Alcohols such as methanol, ethanol, and propanol, can be used for transesterification reaction without any significant difference in the yield of the product. Methanol is toxic but is preferred because of its low cost. Ethanol is not preferred because of its low reactivity compared to methanol but viscosity of ethyl esters is slightly higher and cloud point and pour point are slightly lower than methyl esters [18] However, methanol has a lower boiling point and the transesterification reaction is carried out at this temperature. The commonly employed molar ratio for two-step transesterification is 6:1 for acid-catalyzed transesterification and 9:1 for base-catalyzed transesterification. However, the optimum molar ratio has shown to differ a little depending on the types of oil and its acid value. For single step transesterification reaction, 10:1 molar ratio has been used more often, although an

optimum molar ratio varying from 6:1 to 13:1 has been studied. A molar ratio higher than the optimum value reduces the yield and makes the separation problem. High molar ratio (40:1) is needed where supercritical methanol is used for transesterification method [19]. The excess methanol used in the reaction can be recovered for reuse to reduce the material cost.

2.3.1.4 Type of catalyst

A catalyst is needed to improve the transesterification reaction and yield. Catalysts are classified as acid, base and enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed process. However, acid-catalyzed process is more suitable if the oil has high free fatty acid and water content [20]. Homogeneous catalyst has been in use at industrial level for production of biodiesel. Sulphuric acid is the commonly used catalyst during acid-catalyzed process whereas sodium hydroxide and potassium hydroxide are the catalyst used for base-catalyzed process. The homogeneous catalysts have to be removed from the final product with repeated washing with distilled water that cause wastewater [21]. Therefore, heterogeneous catalysts have been tried to overcome the drawbacks of homogeneous catalysts. Heterogeneous catalysts can be separated from the reaction mixtures and reused and also show less corrosive that make them better than homogeneous catalyst.

2.3.1.5 Reaction temperature

The commonly employed temperature ranges from room temperature to up to 65 ^{o}C. Temperature positively influenced the reaction rate and yield of esters with increase in temperature. The boiling point of methanol is 64.7 ^{o}C so the transesterification reaction is carried out within this range as a temperature higher than this may burn methanol. Higher temperature must be avoided because the saponification can occur [22]. Temperature of 350 ^{o}C has been considered to be optimum while using supercritical methanol.

2.3.1.6 Reaction time

The conversion rate increases with reaction time. Freedman et al.[23] synthesized biodiesel from peanut, cottonseed, sunflower and soybean oils under the

condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the 93±98% conversions were obtained from all four oils. The effect of reaction time on transesterification of beef tallow with methanol was studied. The reaction was very slow at the first minute. From one to five minutes, the reaction proceeded very fast as the apparent yield of methyl esters increased from 1 to 38 and the production slowed down and reached the maximum value at about 15 minutes.

2.3.2 Type of catalyst

2.3.2.1 Acid catalyst

The processes are catalyzed by Br∅nsted acids such as sulfuric acid, sulfonic acid and hydrochloric acid, but the most commonly used is sulfuric acid [23]. These catalysts give very high yields in alkyl esters but the reactions are slow and requiring high temperature and more than one day to give the high conversion [1, 24]. Transesterification process under acid-catalyzed condition needs to be done in absences of water because the water reduces the yield alkyl ester. The alcohol:oil molar ratio is one of the main factors that influence the transesterification. An excess alcohol favors the formation of products but also makes the recovery of glycerol difficult.

2.3.2.2 Base catalyst (Alkaline catalyst)

The base-catalyzed transesterification of vegetable oils proceeds faster and less corrosive than the acid-catalyzed reaction. The alkaline catalysts including hydroxides, carbonates and alkoxides are often used commercially especially sodium and potassium hydroxide. Sodium methoxide and potassium methoxide are the other homogeneous catalyst that better than sodium hydroxide and potassium hydroxide in terms of yield. Formation of small amount of water during the transesterification reaction results in lower yield of biodiesel with sodium hydroxide or potassium hydroxide as a catalyst while sodium methoxide and potassium methoxide give higher yield because there is no water formation as by-product during the reaction [20, 25].

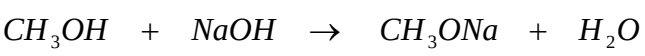

Figure 2.3 The reaction of sodium methoxide

This process gives very high yields in short reaction times and relatively cheap, but it has disadvantage, the process is added these catalysts into feedstocks, the FFAs can react with the catalyst to form soap and water if the oil or fat contains amounts of FFAs. The reaction was showed below:

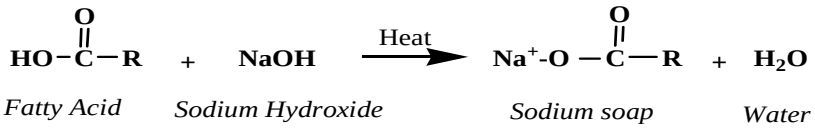

Figure 2.4 The reaction of sodium soap [8]

This reaction is called “saponification”. So glyceride and alcohol must be anhydrous because the water will change the reaction to saponification. The presence of soap effect to yield of esters and makes the separation problem.

2.3.2.3 Lipase catalyst

The use of lipase catalyst is unfavourable compared to using base catalyst in transesterification process but immobilized lipase in esterification process has the advantage, the yield of ester are almost 100% and no problem with contaminated glycerol [19]. The few advantages of using lipase catalysts can tolerate organic solvents, are stable and readily available. The example of lipase catalysts includes PS 30 [26] and Novozym 435-catalyzed [27-28]. Immobilized *Pseudomonas fluorescence* lipase is a biocatalyst that very popular because its activity is more effective and it can be repeatedly used without any decrease activity [29].

2.3.2.4 Non-ionic base catalyst [30]

The organic bases has been developed and used as catalyst or reactant for organic synthesis. These provide for a mild reaction condition to simplify manipulation of the factors involved in increasing the yield of the ester. Bases are frequently used in this process including amines such as triethylamine, piperidine and pyridine; amidines such as 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); guanidines such as 1,5,7-

triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,1,2,3,3-pentabutylguanidine (PBG) and triamino phosphoranes such as tert-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorane (BEMP).

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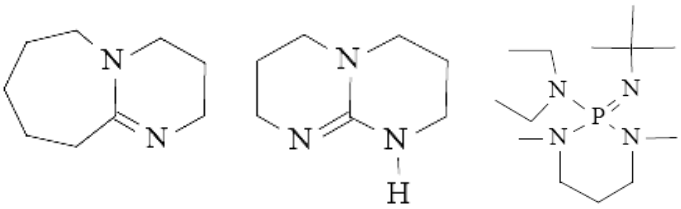

DBU **TBD** **BEMP**

Figure 2.5 Samples of non-ionic base-catalysts

2.3.2.5 Heterogeneously catalyst

Although transesterification using base-catalyzed process gives high conversion in short times, the reaction has many disadvantages, for example, it is energy intensive, catalyst has to be removed from the product, recovery of glycerin is difficult, alkaline waste-water requires treatment and FFAs and water interfere with reaction. To solve the problems, attempts to use heterogeneous catalyst system in alcoholysis of triglycerides have been investigated. They can be easily removeded at the end of the reaction and could also be reused even they could not be used for a long duration of time as they leach out and the reaction is incomplete and the phases are difficult to separate. However, the performance is still unfavourable compared to the based catalysts. There are many heterogeneous catalysts have been used such as zeolites, clays, alumina, ion exchange resins, oxides, etc [31]. Activated calcium oxide (CaO) was used as solid-based heterogeneous catalyst for eight times without significant deactivation. Magnesium oxide, successfully used as catalyst for biodiesel development was found to be cost effective also.

2.3.2.6 Noncatalytic transesterification process

With the aim of developing a novel transesterification process without using the catalysts, the process using supercritical fluids has been investigated. Supercritical alcohols have been explored as a reactant for the transesterification

process and have proven a conversion rate of triglyceride to be 80-100% as called non-catalytic transesterification process. This process can also be done without the aid of a catalyst, high temperature, high pressure and less excess alcohol is required in absence of catalysts [32].

The advantages and disadvantages of each process can be summarized as in Table 2.1

Table 2.1 Comparison of the different technologies to produce biodiesel [1]

	Acid	Base	Lipase	Supercritical alcohol
Reaction temperature(^{o}C)	55-80	60-70	30-40	239-385
FFA in raw materials	Ester	Soap	Ester	Ester
Water in raw materials	Influence	Influence	No influence	
Yield of Esters	Normal	Normal	Higher	Good
Recovery of glycerol	Difficult	Difficult	Easy	
Purification of ester	Washing	Washing	None	
Cost of catalyst	Cheap	Cheap	Expensive	Medium

2.4 Biodiesel quality

Biodiesel is made up of various types of fatty acids, which are transformed into fatty acid methyl esters by transesterification. Different fractions of each type of fatty acid methyl esters present in various feedstocks influence some properties of fuels. When compared properties of diesel fuel and biodiesel, there is a standard for describing the chemical composition and purities of fatty acid methyl ester as shown in Table 2.2. For Thailand, it has set legislative assembly characteristic and quality of biodiesel as shown in Table 2.3.

Table 2.2 Comparison of fuel properties between diesel and biodiesel [33]

Fuel property	**Diesel**	**Biodiesel**
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131,295	117,093
Viscosity, at 40° C	1.3-4.1	1.9-6.0
Specific gravity kg/l at 60° F	0.85	0.88
Density, lb/gal at 15° C	7.079	7.328
Water content	161 ppm	0.05 %wt
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. wt %	0	11
Sulfur, wt %	0.05	0.0 - 0.0024
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air/fuel ratio wt./wt.	15	13.8
BOCLE Scuff, grams	3,600	>7,000

Table 2.3 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand [34]

Characteristic	Value	Method of standard
Methyl ester, %wt.	>96.5	EN 14103
Density at 15^{o}C, kg/m^{3}	860-900	ASTM D 1298
Viscosity at 40^{o}C, cSt	3.5-5.0	ASTM D445
Flash point, ^{o}C	>120	ASTM D 93
Carbon residue, on 10% distillation residue, %wt	<0.30	ASTM D 4530
Cetane number	>51	ASTM D 613
Sulfur, %wt.	<0.0010	ASTM D 2622
Sulfated ash, %wt.	<0.02	ASTM D 874
Water, %wt.	<0.050	ASTM D 2709
Total contaminate, %wt.	<0.0024	ASTM D 5452
Copper strip corrosion	<96.5	ASTM D 130
Oxidation stability at 110^{o}C, hours	>6	EN 14112
Acid value, mg KOH/g	<0.50	ASTM D 664
Iodine value, g Iodine/100 g	<120	EN 14111
Linolenic acid methyl ester, %wt.	<12.0	EN 14103
Methanol, %wt.	<0.20	EN 14110
Monoglyceride, %wt.	<0.80	EN 14105
Diglyceride, %wt.	<0.20	EN 14105
Triglyceride, %wt.	<0.20	EN 14105
Free glycerin, %wt.	<0.02	EN 14105
Total glycerin, %wt.	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorus, %wt.	<0.0010	ASTM D 4951

1. Viscosity

Viscosity is an important property of any fuel because it is an indication of the ability of a material to flow. Too high a viscosity and the injectors do not perform properlyThe kinematic and dynamic viscosity of biodiesel is determined by ASTM D 445.

2. Flash Point

Flash point is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame. The flash point of biodiesel should be at least 120 ^{o}C, and in general, it is higher than diesel fuels so biodiesel is a safer fuel than diesel. Flash point of biodiesel is determined by ASTM D 93.

3. Carbon residue

Carbon residue is the part remaining after a sample has been subjected to combustion. This is particularly important in diesel engines because of the possibility of carbon residues clogging the fuel injectors. ASTM D 4530 is the standard test method for determination of carbon residue and the maximum limit for carbon residue in biodiesel is 0.050% by mass.

4. Cetane number

The cetane number can be defined as a measurement of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in a standardized engine test. The cetane number of biodiesel is determined by ASTM D 613. The cetane number for biodiesel should be a minimum of 51 but too high cetane number can lead to engine problems. The cetane number of B100 can be accurately predicted using the ester’s composition.

5. Total sulfur

Low sulfur helps both environment and engine life. Total sulfur in biodiesel is determined by ASTM D 2622. This test is an indicator of contamination of protein material or catalyst material or neutralization material from the production process.

6. Sulfate ash

Sulfate ash content describes the residue remaining after a sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. Sulfated ash in biodiesel is determined by ASTM D 874. This test is an indicator of the quantity of residual metals in the biodiesel that came from the catalyst used in the esterification process.

7. Water and sediment

Water and sediment determines the volume of free water and sediment in fuels having viscosities at 40 °C in the range 1.0 to 4.1 mm2/s and densities in the range of 700 to 900 kg/m^3. Water and sediment in biodiesel tend to disrupt fuel handling, poor combustion, plugging and smoking and also cause fouling in the fuel system of an engine. Moreover, water can support microbial growth in storage tanks.

8. Acid number

The acid number is a measure of the amount of acidic substances in a fuel that is a direct measure of free fatty acids in biodiesel. The acid number can provide an indication of the level of lubricant degradation while the fuel is used. It can become a serious issue when high free fatty acids feed stocks are used to produce biodiesel.

9. Free and total glycerin

Glycerol can be free or bonded, free glycerol is the amount of glycerol not in glyceride bonds and bonded glycerol is the amount of glycerol in mono-, di- and triglyceride bonds. Total glycerol is the sum of free and bonded glycerol. Free and total glycerin content in biodiesel is determined by EN 14105. Fuel that contaminate with free glycerol will usually have problems with glycerol settling in storage tanks, creating a viscous mixture that can plug fuel filters and cause combustion problems engines. Moreover, high glyceride content will increase viscosity and carbon residue of biodiesel.

10. Phosphorus

This test covers the quantitative determination of barium, calcium, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and

additive packages. Phosphorus in biodiesel can come from incomplete refining process of the vegetable oil and from bone and proteins encountered in the rendering process.

2.5 Solvent extraction [35]

Solvent extraction is the traditional term of liquid-liquid extraction that involves the distribution of a solute between two immiscible liquid phases in contact with each other. This method uses to separate a substance selectively from a mixture, or to remove the impurities from a solution. Solvent extraction is based on the transfer of a solute from one liquid phase into another liquid phase. The success of this method depends upon the difference in solubility of a compound in various solvents. In the practical use, usually one phase is water or aqueous solution and the other an organic solvent which is immiscible with water.

The organic phase often settles as the upper layer because it has a lower density than water, but the opposite situation also occurs. A solute A, which initially is dissolved in one of the two liquids, eventually distributes between the two phases. When this distribution reaches equilibrium, the solute has one concentration $[A]_{aq}$ in the aqueous phase and another concentration $[A]_{org}$ in the organic phase.

Solvent extraction is used in numerous chemical industries to produce pure chemical compounds ranging from pharmaceuticals and biomedicals to heavy organics and metals, in analytical chemistry and in environmental waste purification.

2.6 Adsorption [36-37]

Adsorption is a process that uses a solid to remove particles from a liquid or gas that passes across it. The particles stick to its surface. Adsorption has been known for thousands of year and they are increasingly utilised to perform desired bulk separation or purification purposes. The heart of the adsorption process is usually a porous solid medium. The use of porous solid is simply that it provides a very high surface area or high micropore volume and it is this high surface area or micropore volume that high adsorptive capacity can be achieved.

The adsorption separation is based on three mechanisms including steric, equilibrium and kinetic mechanisms. In the steric mechanism, the porous solid has

pores having dimension such that it allows small molecules to enter while excluding large molecules from entry. The equilibrium mechanism is based on the solid having different ability to accommodate different species, that is the stronger adsorbing species is removed by the solid. The kinetic mechanism is based on the different rates of diffusion of different species into the pore; thus by controlling the time of exposure the faster diffusing species is preferentially removed by the solid.

Adsorption can be divided into two types:

2.6.1 Physisorption

Physisorption is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. The phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive.

2.6.2 Chemisorption

Chemisorption is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. The molecules undergo a chemical bonding with the molecules of the solid, and this attraction may be stronger than the force holding the solid together. They may form different compounds if the molecules are removed.

2.7 Adsorbents [36-37]

The porous solid of a given adsorption process is a critical variable. The success or failure of the process depends on how the solid performs in both equilibria and kinetics. A solid with good capacity but slow kinetics is not a good choice as it takes adsorbate molecules too long a time to reach the particle interior. This means long gas residence time in a column, hence a low throughput. On the other hand, a solid with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. Thus, a good solid is the one that provides good adsorptive capacity as well as good kinetics. To satisfy these two requirements, the

solid must have high surface area or micropore volume, and the solid must have relatively large pore network for the transport of molecules to the interior

To satisfy the first requirement, the porous solid must have small pore size with a reasonable porosity. This suggests that a good solid must have a combination of two pore ranges including the micropore range and the macropore range. The classification of pore size as recommended by IUPAC is often used to delineate the range of pore size: micropores ($d < 2$ nm), mesopores (2 nm $< d < 50$ nm) and macropores ($d > 50$ nm).

This classification is arbitrary and was developed based on the adsorption of nitrogen at its normal boiling point on a wide range of porous solids. Most practical solids commonly used in industries do satisfy these two criteria, with solids such as activated carbon, clay, zeolite, alumina and silica gel. The industries using these solids are diversified, with industries such as chemical, petrochemical, biochemical, biological, and biomedical industries.

2.7.1 Silica gel

Silica gel is the synthetic amorphous silica. It is a hard glassy substance and is milky white in color. Silica gel is a rigid and continuous network of spherical particles of colloidal silica. This adsorbent is used in most industries for water removal due to its strong hydrophilicity of the silica gel surface towards water. Some of the applications of silica gel are water removal from air, drying reactive and non-reactive gases, adsorption of hydrogen sulfide, oil vapour and alcohols

Silica gel is synthesized by mixing a sodium silicate solution with a mineral acid such as hydrochloric or sulfuric acid. The reaction generates a finely particles of hydrate SiO_2 that known as silica hydrosol or silicic acid. The hydrosol polymerizes into a white jellylike precipitate, which is silica gel. Depending on the conditions of preparation, silica gel has a wild range of properties such as surface area, pore volume and strength. Two types of silica gel are known as regular-density and low-density silica gel. The regular-density silica gel has a surface area of 750-850 m^2/g and average pore diameter of 22-26 Å, while the low-density silica gel gel has a surface area of 300-350 m^2/g and average pore diameter of 100-150 Å.

2.7.2 Activated carbon

Activated charcoal is the most commonly used adsorbent. It is full of holes, which makes its total surface area very large. There is lots of surface to holes molecules, which remain in place by van der Waals forces (physisorption). The raw materials for activated carbon are wood, peat, coals, petroleum coke, bones, coconut shell and fruit nuts. Anthracite and bituminous coals have been the major sources. After initial treatment and pelletizing, one activation process involves cabonization at 400-500 ^{o}C to eliminate the bulk of the volatile matter and then partial gasification at 800-100 ^{o}C to develop porosity and surface area. The product is used for aqueous or gas purpose. The inorganic material contain in activated carbon is measure as ash content, generally in range between 2 and 10%

Macropore having a size range of greater than 100 nm is normally not filled with adsorbate by capillary condensation (except when the reduced pressure is approaching unity). The volume of macropore is usually in the order of 0.2-0.5 cc/g and the area contributed by the macropore is usually very small, of the order of 0.5 m^2/g, which is negligible compared to the area contributed by the micropore. Macropores, therefore, are of no significance in terms of adsorption capacity but they act as transport pores to allow adsorbate molecules to diffuse from the bulk into the particle interior.

Mesopore has a size range from 2 nm to 100 nm, and it is readily filled during the region of capillary condensation (P/Po > 0.3). The volume of mesopore is usually between 0.1 to 0.4 cc/g and the surface area is in the range of 10-100 m^2/g. Mesopore contributes marginally to the capacity at low pressure and significantly in the region of capillary condensation. Like macropores, mesopores act as transport pore when capillary condensation is absent and they act as conduit for condensate flow in the capillary condensation region.

Micropores are pores having size less than 2 nm. These pores are slit-shaped and because of their high dispersive force acting on adsorbate molecule they provide space for storing most of adsorbed molecules and the mechanism of adsorption is via the process of volume filling.

2.7.3 Clay minerals [38]

Clay minerals are layer silicates that are formed usually as products of chemical weathering of other silicate minerals at the earth's surface. They are found

most often in shales, the most common type of sedimentary rock. In cool, dry, or temperate climates, clay minerals are fairly stable and are an important component of soil. Clay minerals act as "chemical sponges" which hold water and dissolved plant nutrients weathered from other minerals. Clay has many uses today including, pottery, ceramic, lining for landfills, computer chips, cosmetics and pharmaceuticals. Clay minerals are important because of the negative charge they contribute for cation exchange. So, they act as “chemical sponges” which hold and dissolved plant nutrients weathered from other minerals. They have the ability to attract water molecules at surface area (because the ion and water is not attracted sink inside the clay). For prehistoric times, clay has been essential in industry architecture and agriculture. There are many types of known clay minerals. Some of the more common types are Kaolinite, Smectite and Vermiculite. Kaolinite is the mineral name for kaolin or china clay. It is economically important in the ceramic and paper industries. It has a white, powdery appearance. Smectite or bentonite is the chief constitutent of fuller’s earth, and is also used in drilling muds (muds used cool and lubricate drilling equipment). This clay mineral is the weathering product of mafic silicates, and is stable in arid, semi-arid, or temperate climates. It has the ability to adsorb large amounts of water, forming a water-tight barrier. Vermiculite (similar to smectite) will expand on heating to produce a material used in insulation. This clay mineral has the ability to adsorb water, but not repeatedly. It is used as a soil additive for retaining moisture in potted plants, and as a protective material for shipping packages.

Especially adsorbent, Bentonite is used very in the oil industry as drilling muds to protect the cutting bit while drilling, filtering and deodorizing agents in the refining of petroleum.

2.8 Literature review

In 1997, Munson *et al*. [6] reported the process for treating cooking oil or fat with magnesium silicate and at least one alkaline material including calcium hydroxide, calcium oxide and magnesium oxide. The result showed that the free fatty acid content in the oil could be reduced by using the adsorbents and this method improved extension of the life of the cooking oil employed in restaurant and industrial frying operations.

In 2003, Kumar *et al*. [3] synthesized biodiesel from vegetable oil and animal fats in presence of NaOH and H_2SO_4 at 60-80 ^oC. The transesterification was affected by the mode of the reaction, molar ratio of the glycerides to alcohol, type and quality of catalyst, reaction time, reaction temperature and purity of oil and fats. Under 6:1 molar ratio of methanol to oil, 1 hour of reaction and 60 ^oC of temperature, the conversion of 93-98% was achieved.

In 2004, Van Gerpen *et al*. [39] studied the method to removed soap and glycerin from biodiesel produced from soybean oil and yellow grease by using Magnesol R60 compared with water washing process. The found that the amount of soap and free and total glycerin in biodiesel by using Magnesol R60 less than water washing process. Moreover, this process reduced the water usage, wastewater treatment, and the additional processing steps needed to separate the emulsion.

In 2005, Bertram *et al*. [7] purified biodiesel synthesized from soybean oil and yellow grease by using at least one adsorbent including magnesium silicate. Impurities such as soap, is formed during the transesterification which the base-catalyst is present to speed the reaction. When a large amount of soap is present, the water-washing causes emulsion problems, so water-washing does not effectively get rid some of the other contaminants. They found that magnesol could reduce imurities including soap and metal and also improve oxidative stability of biodiesel.

In 2006, Charoensinvorakul [38] studied the method to reduced free fatty acid in biodiesel produced from crude palm oil by using adsorbents such as magnesol, activated charcoal, basic alumina, molecular sieve, bentonite clay and NaOH-treated bentonite clay. The result showed that the activated charcoal and magnesol could reduce free fatty acid from 0.184 to 0.014% and 0.016%, respectively.

In 2008, Mazzieri *et al*. [40] studied adsorption of silica gel for glycerol in biodiesel containing only fatty acid methyl esters or samples spiked with contaminants including water, methanol, monoglyceride and soap. The results showed that silica gel was very efficient for adsorption of glycerol and monoglyceride. Adsorption of glycerol was not influenced by small amount of water and soap but it was reduced by the presence of monoglyceride and methanol.

In 2009, Banavali *et al*. [41] reported the method for purification of crude glycerol derived from biodiesel production using alkaline catalysts. The method comprised combining the crude glycerol with acid, separating a glycerol layer, and treating the glycerol layer to decolorize it. They used sulfuric acid to neutralize basic salts in crude glycerol that gave three layers: the upper layer rich in fatty acids and fatty acid esters, the middle layer rich in glycerol, and the bottom layer rich in salts. The glycerol layer was separated using gravity settler or centrifuge.

In 2010, Hayyan *et al*. [42] reported the method for separating glycerin palm oil-based biodiesel using ionic liquids. They used the mixture of quaternary ammonium salt (choline chloride) and glycerol as a solvent and the 1:1 ratio of choline chloride: glycerol gave the best extraction yield. Moreover, they found that the ratio of biodiesel to solvent was more important than the solvent composition ratio in affecting the extraction efficiency and the ratio of 1:1 gave the best result.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1 Chemicals and materials

1. 2-Propanol: commercial grade;
2. Acetic acid: analytical grade; Merck
3. Bromophenol blue: analytical grade; Carlo erba
4. Ethyl acetate: analytical grade; Merck
5. Glacial acetic acid: analytical grade; Merck
6. Heptane: analytical grade; Merck
7. Hexane: analytical grade; Lab-Scan
8. Methanol: analytical grade; Merck
9. Sodium hydroxide: analytical grade; ACS
10. Ferric sulfate (Iron(III) sulfate): analytical grade; Carlo erba
11. Potassium chloride: analytical grade; Merck
12. EN 14105 standard and internal standard solution; Supelco
13. N-methyl-N-(trimethylsilyl)-trifluoroacetamide: derivatization grade; Sigma-Aldrich
14. Refined palm oil
15. Sodium chloride
16. Activated carbon
17. Activated clay
18. Silica gel 60 for column chromatography; Merck

3.1.2 Equipments

1. Gas Chromatography: Varian CP-3800, USA
2. Rotary evaporator: Buchi R-200, Germany
3. Water bath and shaker: Mammert W350, Germany
4. Viscometer: Tamson TV 4000, Holland
5. Atomic absorption spectrometer: Perkin Elmer AAnalyst 100, USA

3.2 Procedure

3.2.1 Preparation of the saturated salt solutions

Five hundred milliliters of water was added into a 1000-ml beaker and heated to 50 ^{o}C. Then, sodium chloride (NaCl) was added until the solution was saturated. The same method was also used for preparation of saturated salt solution of potassium chloride (KCl) and ferric sulfate ($Fe_2(SO_4)_3$).

3.2.2 Synthesis of biodiesel

Five hundred grams of palm oil was weighed into a 1000-ml two-necked round bottom flask equipped with a reflux condenser and thermometer. After the oil was heated to 60 °C, the solution of sodium hydroxide (5.0 g) in methanol (144.8 mL) was slowly added into the reaction then the mixture was heated to 60 °C and stirred for 1.5 hours. The mixture was transferred to a separatory funnel and allowed to stand for 30 minutes then glycerin layer at the bottom was removed to give crude biodiesel 505 grams.

3.2.3 Purification of crude biodiesel by using the saturated salt solutions

3.2.3.1 Type of saturated salt solution

Three types of saturated salt solution (including NaCl, KCl and $Fe_2(SO_4)_3$) were studied. After glycerin layer was separated, 50 milliliters of biodiesel was washed with saturated salt solution at 1:1 ratio of biodiesel and saturated salt solution, then agitated for 30 seconds at room temperature and left for settling for 30 minutes. The upper layer was collected and filtered. The amount of soap content was determined by titration method according to 3.2.6.1.

3.2.3.2 Shaking time

Fifty milliliters of each biodiesel from 3.2.2 was washed three times with saturated salt solution (NaCl) at 1:1 ratio of biodiesel and saturated salt solution, then agitated for 30 seconds, 1 and 3 minutes at room temperature and left for settling for 30 minutes. The upper layer was collected and filtered. The amount of soap content was determined by titration method according to 3.2.6.1.

3.2.3.3 Ratio between biodiesel and saturated salt solution

Fifty milliliters of biodiesel from 3.2.2 was washed with saturated salt solution (NaCl) at the 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1 and 1:2 ratio of biodiesel and saturated salt solution, then agitated at room temperature and left for settling for 30 minutes. The upper layer was collected and filtered. The amount of soap content was determined by titration method according to 3.2.6.1.

3.2.3.4 Temperature of washing

Fifty milliliters of biodiesel from 3.2.2 was washed three times at 50 ^{o}C and room temperature with saturated salt solution (NaCl) at the ratio of biodiesel and saturated salt solution obtained from 3.2.3.3, and left for settling for 30 minutes. The upper layer was collected and filtered. The amount of soap content was determined by titration method according to 3.2.6.1.

3.2.3.5 Methanol content in crude biodiesel

After glycerin layer was separated, methanol in crude biodiesel was removed by using rotary evaporator. Then, 50 milliliters of biodiesel was washed with NaCl saturated salt solution at 10:1, 5:1 and 1:1 ratio of biodiesel and saturated salt solution, then agitated at room temperature and left for settling for 30 minutes. The upper layer was collected and filtered. The amount of soap content was determined by titration method according to 3.2.6.1.

3.2.4 Purification of crude biodiesel by using adsorbents

Three types of adsorbents (including silica gel, activated carbon and activated clay) were studied. After biodiesel was washed with the NaCl saturated salt solution, 50 grams of biodiesel was treated with each of 0.1% (w/w) of adsorbents at room temperature with stirring rate at 150 rpm for 10 minutes and the adsorbents were removed by filtration. The biodiesel was subjected to determine the soap content by titration method according to 3.2.6.1, free and total glycerin contents were determined according to 3.2.6.2 and sodium contents were determined by using Atomic absorption spectrometer.

3.2.5 Purification of crude biodiesel by using water washing

After biodiesel was washed with the NaCl saturated salt solution, 50 grams of biodiesel was washed with water in a separatory funnel until the washed water became clear. The biodiesel was subjected to determine the soap content by titration method according to 3.2.6.1, free and total glycerin contents were determined according to 3.2.6.2 and sodium contents were determined by using Atomic absorption spectrometer compared with 3.2.5 and conventional water washing process, 50 milliliters of biodiesel was successively washed with water in a separatory funnel until the washed water became clear.

3.2.6 Biodiesel analysis

3.2.6.1 Determination of the soap content

Ten grams of biodiesel sample was dissolved in 100 ml of isopropyl alcohol with 2 ml of 1% phenolphthalein as an indicator. The mixture was titrated with 0.01N hydrochloric acid until the color of the solution changed from red to clear color. This amount of 0.01N hydrochloric acid solution is referred as “A”.

Then, 1 ml of 0.04% bromophenol blue was added into the mixture solution and titrated with 0.01N hydrochloric acid until the color of the solution changed from blue to yellow. This amount of 0.01N hydrochloric acid solution is referred as “B”.

The amount of unreacted catalyst was calculated by using the equation (1):

$$g\ of\ catalyst\ /\ g\ of\ sample = \frac{A \times 0.01 \times 40.0}{W \times 1000} \quad (1)$$

Where: A = volume of hydrochloric acid used in first step (mL)

W = weight of untreated biodiesel used (g)

40.0 = molecular weight of sodium hydroxide

And the soap content in the biodiesel was calculated by using the equation (2):

$$Soap\ content\ (ppm) = \frac{B \times 0.01 \times 303.4}{W \times 1000} \quad (2)$$

Where: B = volume of hydrochloric acid used in second step (mL)

W = weight of untreated biodiesel (g)

303.4 = average molecular weight of soap

3.2.6.2 Determination of free and total glycerin (EN14105)

Free and total glycerin contents were determined by using CP-3800 Varian gas chromatograph equipped with an on-column injector and a flame ionization detector (FID). The column was a Glycerides Ultimetal (Varian), 10 m x 0.32 mm (ID) x 0.1 μm (film thickness) with retention gap 2 m x 0.53 mm (ID).

One hundred milligrams of biodiesel sample was accurately weighed (± 0.1 mg) into a 10 mL vial, then, 80 μL of Internal Standard 1, 100 μL of internal standard 2 and 100 μL MSTFA were added to the sample vial, shaken vigorously and stood at room temperature for 15-20 minutes. Approximately 8 mL of heptane was added, then, 1 μL of the mixture was injected into the gas chromatograph at an oven temperature of 50 °C. After held for 1 min, the oven was set to heated at 15 °C/min to 180 °C, at 7 °C/min to 230 °C, and at 10 °C/min to 370 °C (held for 5 min). A carrier gas was helium that used at a flow rate of 4 mL/min. The detector temperature was set to 380 °C and the total run time was 36 minutes.

3.2.6.3 Determination of sodium content

Sodium content was determined by using AAnalyst 100, Perkin Elmer atomic absorption spectrometer. The standard curve of sodium ion was plotted between intensity and concentration using the concentrations of sodium standard solution at 0.1, 0.5, 1, 3 and 5 ppm.

Ten grams of biodiesel was added into a vial contained 10 g of milliQ water, then agitated and allowed to stand for 30 minutes. The milliQ water layer was collected and sodium content was determined.

3.2.6.4 Determination of the properties of biodiesel

The physical properties of biodiesel were determined according to the test methods shown in Table 3.1.

Table 3.1 Test method of biodiesel fuels

Property	Method
Viscosity at 40 °C (mm^2/s)	ASTM D445
Flash point (°C)	ASTM D93
Acid number (mg KOH/g)	ASTM D974
Ester content (%wt)	EN 14103

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Purification of crude biodiesel by using the saturated salt solutions

4.1.1 Effect of type of saturated salt solution

Three types of saturated salt solution including NaCl, KCl and $Fe_2(SO_4)_3$ were investigated. Soap content remained in biodiesel was determined and the results were shown in Table 4.1

Table 4.1 Soap content and acid value of biodiesel washed with three types of saturated salt solution.

Type of salt	Soap content (ppm)	Acid value (mg KOH/g)
Before washing	3539	ND
NaCl	28	ND
KCl	55	ND
$Fe_2(SO_4)_3$	ND*	0.603

*Not detected

When the crude biodiesel was washed with saturated salt solution (NaCl), the mixture was separated into three layers, the upper layer was biodiesel, the middle layer was precipitated glycerin and the lower layer consisted of the saturated salt solution, methanol and sodium hydroxide. While the crude biodiesel was washed with saturated salt solution (KCl and $Fe_2(SO_4)_3$), the mixture was only separated into two layers.

The results from Table 4.1 showed that the soap content in biodiesel could be effectively reduced by saturated salt solution (NaCl and KCl) from 3539 ppm to 28 ppm and 55 ppm, respectively. The soap content after washing with saturated salt solution ($Fe_2(SO_4)_3$) was unable to determine because the solution was highly acidic, therefore, soap was change into free fatty acid and dissolved in biodiesel layer. Due to

this phenomenon, the acid value was measured instead. The acid value of biodiesel washed with saturated salt solution ($Fe_2(SO_4)_3$)was equal to 0.603 mg KOH/g, which exceeded the biodiesel standard value of 0.5 mg KOH/g [34].

This study could be concluded that saturated salt solution (NaCl) was the most suitable type of salt for further experiments since it gave lowest soap content and also most cost effective. Moreover, it could be observed that the layer of the saturated salt solution (NaCl) was clear, therefore, the emulsion was not generated with this saturated salt solution.

4.1.2 Effect of the shaking time

The effect of the shaking time was studied at 30 seconds, 1 and 3 minutes, respectively. The conditions were 1:1 ratio of biodiesel and saturated salt solution (NaCl) at room temperature. The results were shown in Figure 4.1.

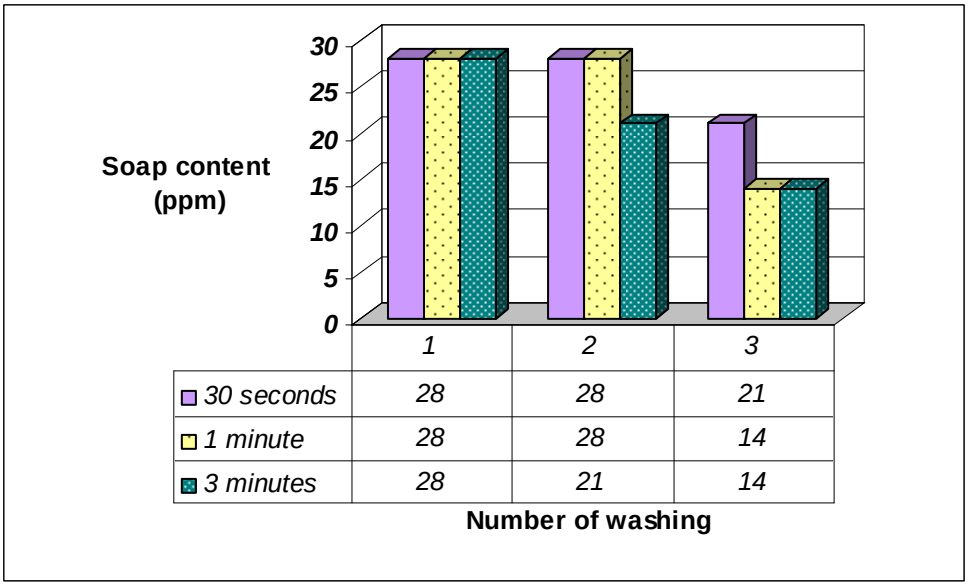

Figure 4.1 Effect of the shaking time on soap content in biodiesel using 1:1 ratio of biodiesel and saturated salt solution (NaCl) at room temperature.

The results from Figure 4.1 showed that the saturated salt solution (NaCl) could be effectively used to remove soap in biodiesel. The soap content was reduced from 3452 ppm to 28 ppm by washing with the saturated salt solution (NaCl) for 30 seconds, 1 minute and 3 minutes, respectively. Therefore, the suitable shaking

time was 30 seconds because all of the shaking times gave the results more or less the same.

The results also showed that only one time washing with the saturated salt solution (NaCl) was sufficient for this purpose.

4.1.3 Effect of the ratio between biodiesel and saturated salt solution

The effect of the ratio between biodiesel and saturated salt solution (NaCl) was studied in 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1 and 1:2 ratio of biodiesel and saturated salt solution. Soap content remained in biodiesel was determined and the results were shown in Figure 4.2.

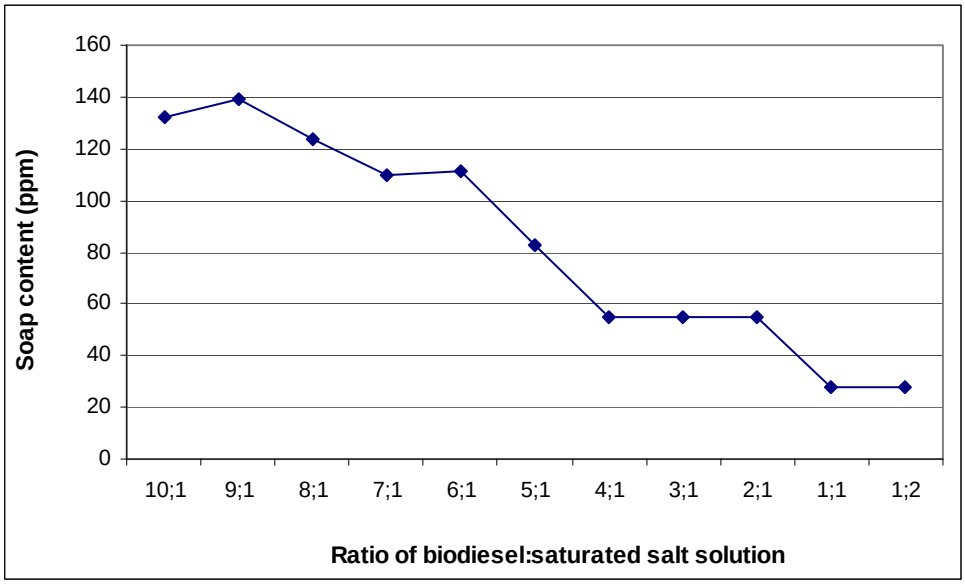

Figure 4.2 Effect of the ratio between biodiesel and saturated salt solution (NaCl) on soap content using 30 seconds of the shaking time at room temperature.

From the results, the soap content could be reduced from 3314 ppm to 28 ppm by using 1:1 and 1:2 ratio of biodiesel and saturated salt solution (NaCl). There was no difference in soap content remained between two ratios, therefore, the optimal ratio between biodiesel and saturated salt solution (NaCl) was 1:1.

4.1.4 Effect of temperature of washing

The effect of temperature was investigated at room temperature and 50 ^{o}C and the results were given in Figure 4.3.

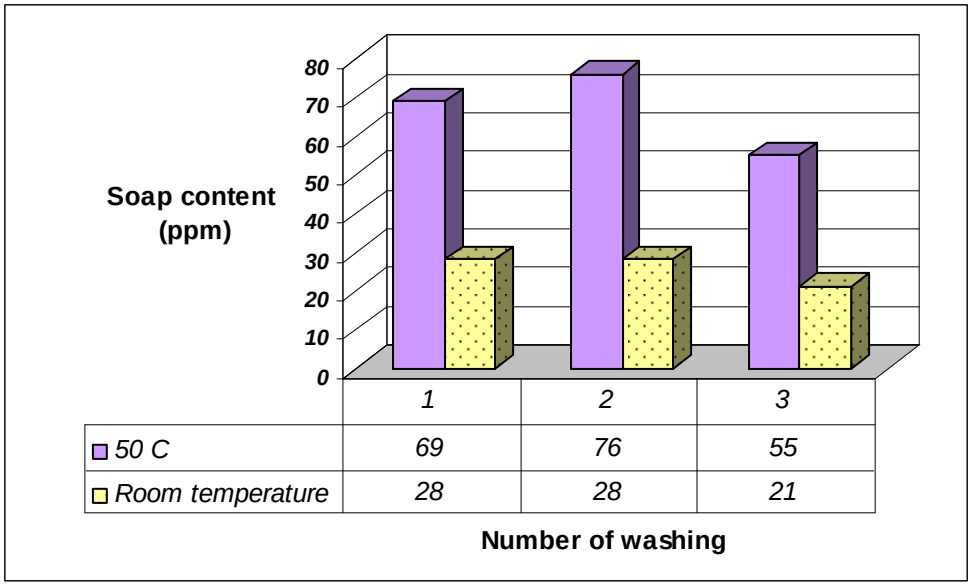

Figure 4.3 Effect of temperature of washing on soap content using 1:1 ratio of biodiesel and saturated salt solution (NaCl) and 30 seconds of the shaking time.

The results from Figure 4.3 showed that the soap content in biodiesel could be removed by using the saturated salt solution (NaCl) at room temperature better than at 50 ^{o}C. This was due to the solubility of soap in biodiesel in higher temperature was increased. Therefore, the suitable temperature to removed soap was room temperature.

4.1.5 Effect of methanol content in crude biodiesel

The effect of methanol content was investigated. The methanol was removed by using rotary evaporator and 10:1, 5:1 and 1:1 ratio of biodiesel and saturated salt solution (NaCl) was studied at room temperature. The results were given in Table 4.2.

Table 4.2 Soap content of biodiesel after removed methanol and washed with saturated salt solution (NaCl) for 30 seconds at room temperature.

	Soap content (ppm)
Before removing of methanol	3501
After removing of methanol	166
10:1	14
5:1	14
1:1	7

After methanol was removed, the soap content could be reduced from 3501 ppm to 166 ppm. When methanol was removed, soap was subsequently precipitated. The soap content could be reduced from 166 ppm to 14, 14 and 7 by using 10:1, 5:1 and 1:1 ratio of biodiesel and saturated salt solution (NaCl), respectively.

4.2 Purification of crude biodiesel by using adsorbents compared with water washing

4.2.1 Determination of the soap content

Water washing and three types of adsorbents (including silica gel, activated carbon and activated clay) were studied. The results of the soap content in biodiesel were given in Table 4.3.

Table 4.3 Soap content of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing.

	Soap content (ppm)
Washing with salt solution	27.59
Washing with salt solution and water	ND*
0.1% Silica gel	ND
0.1% Activated carbon	ND
0.1 % Activated clay	ND
Water washing	ND

*Not detected

The results showed that the soap content was totally removed by both of process using adsorbents and water washing process. The biodiesel washed with saturated salt solution (NaCl) left small amount of soap content, and this could be eliminated by adsorbents and water washing.

4.2.2 Determination of free and total glycerin

Free and total glycerin contents were determined by using CP-3800 Varian gas chromatograph according to EN 14105. Water washing and three types of adsorbents including silica gel, activated carbon and activated clay were investigated. The results were given in Table 4.4.

Table 4.4 Free and total glycerin contents (%wt) of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing.

	Glycerol	Monoglyceride	Diglyceride	Triglyceride**	Total glycerin
Unwashed biodiesel	0.653	0.415	0.0311	-	0.763
Washing with salt solution	ND*	0.415	0.0312	-	0.111
Washing with salt solution and water	ND	0.387	0.0273	-	0.103
Silica gel	ND	0.308	0.0303	-	0.0828
Activated carbon	ND	0.416	0.0314	-	0.111
Activated clay	ND	0.375	0.0292	-	0.100
Water washing	ND	0.394	0.0280	-	0.105

*Not detected

** Data not available

From GC analysis results, it showed that the free and total glycerin contents of the both biodiesel washed with water and treated with adsorbents were not exceed the limit of the specific biodiesel standard that required glycerol,

monoglyceride, diglyceride, triglyceride and total glycerin less than 0.02, 0.8, 0.2, 0.2 and 0.25 %wt, respectively [34].

It was also found that free glycerol was not found in all of sample because it was removed after washing with saturated salt solution (NaCl). Moreover, only silica gel could reduce monoglyceride content. 26% of monoglyceride could be removed by using 0.1% (w/w) of silica gel.

4.2.3 Determination of sodium content

Sodium content was determined by using atomic absorption spectrometer. The results were shown in Table 4.5.

Table 4.5 Sodium contents of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing.

	Sodium content (ppm)
Washing with salt solution	1.502
Washing with salt solution and water	1.262
0.1% Silica gel	1.262
0.1% Activated carbon	1.352
0.1 % Activated clay	1.244
Water washing	1.212

From Table 4.6, the results showed that the sodium contents of all sample were not exceed the limit of the specific biodiesel standard that required less than 5.0 ppm.

4.3 Properties of biodiesel

Some important properties (including viscosity, flash point, acid number and ester content) were determined. The standard values of these properties were shown in Table 4.6.

Table 4.6 Properties of biodiesel

Property	Biodiesel	Limits	Method
Viscosity at 40 °C (mm^2/s)	4.2 - 4.4	3-5	ASTM D445
Flash point (°C)	>120	>120	ASTM D93
Acid number (mg KOH/g)	0.066 - 0.067	< 0.5	ASTM D974
Ester content (%wt)	94.76	> 96.5	EN 14103

It could be seen that the values of viscosity, flash point and acid number were in range of the specification of biodiesel standard.

From the result, it could be suggested that biodiesel which was washed with saturated salt solution (NaCl) had similar efficiency as compared with water washing process. However, the process using saturated salt solution (NaCl) could reduce wastewater from water washing process. Moreover, only one time washing with the saturated salt solution (NaCl) was sufficient for this purpose. Therefore, the period of time for purifying biodiesel of this process was shorter than water washing process. In addition, the process using saturated salt solution (NaCl) was better than the process by Mayyan *et al*. [42], in which saturated salt solution (NaCl) was cheaper than ionic liquid but gave similar efficiency for removing of glycerin.

CHAPTER V

CONCLUSION

5.1 Conclusion

Purification of biodiesel using adsorbents and saturated salt solution was studied. The biodiesel was synthesized by the transesterification of palm oil with methanol at 6:1 molar ratio of methanol:oil, 1 %wt of sodium hydroxide and reaction temperature of 60°C for 1.50 hours. After the mixture was allowed to stand for 30 minutes, the glycerin layer was separated. The crude biodiesel was subjected to wash with three types of saturated salt solution (sodium chloride, potassium chloride and ferric sulfate) which the saturated salt solution of sodium chloride gave the best result for removal of soap. The effect of the shaking time, the ratio between biodiesel and the saturated salt solution of sodium chloride, temperature of washing and methanol content were studied. The results showed that the optimum conditions were 1:1 ratio of crude biodiesel and saturated salt solution of sodium chloride, one time of washing for 30 seconds at room temperature. By washing crude biodiesel with saturated salt solution of sodium chloride, the soap content could be reduced from 3500 ppm to 28 ppm. The biodiesel washed with the saturated salt solution of sodium chloride was further purified by using adsorbents including silica gel, activated carbon and activated clay. The results showed that the process using adsorbents could reduce the soap content similar to water washing process. Although the values of free and total glycerin content passed the specification of biodiesel standard, monoglyceride and diglyceride could not be reduced by either water washing or adsorbents except silica gel that could reduce 26% of monoglyceride. The biodiesel properties were also determined and the results showed that the values of acid number, viscosity and flash point passed the specification of biodiesel standard. Moreover, the process using the saturated salt solution of sodium chloride could reduce wastewater from water washing process.

5.2 Suggestion

1. New saturated salt solution such as seawater and alkaline earth salt should be investigated for further work.
2. New adsorbents for removing monoglyceride, diglyceride and triglyceride should be studied.

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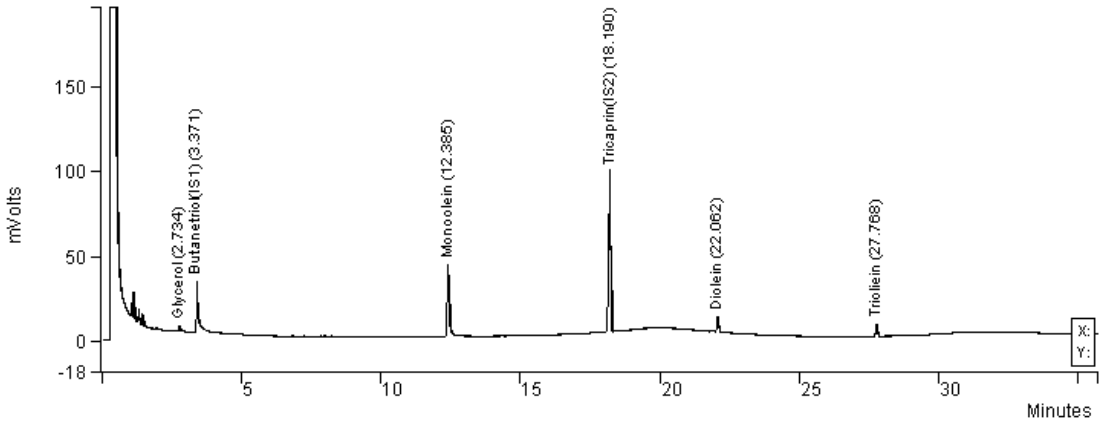
APPENDICES

Appendix A

GC chromatogram

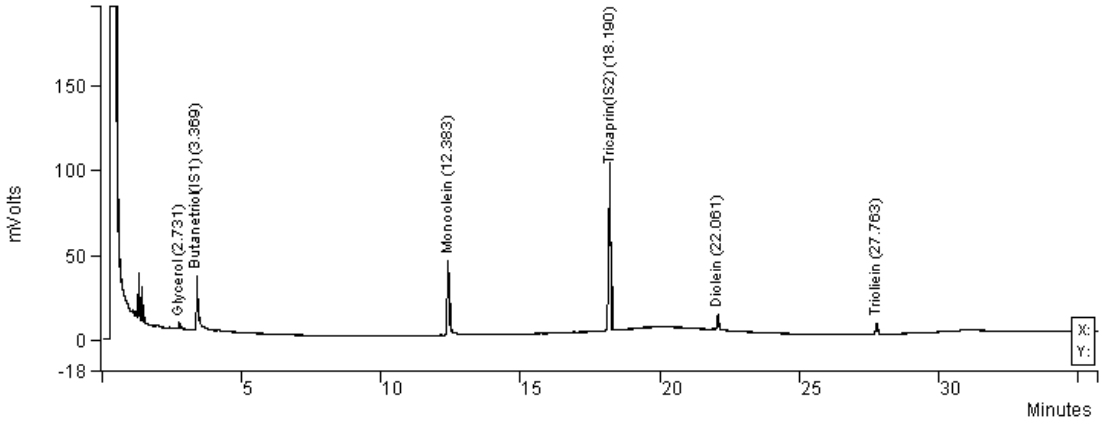
Data File:	c:\star\joe\std1.1 11;30;40 am.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:36:25
Sample ID:	std.1.1	Times Calculated:	4
Operator (Inj):	jo	Calculation Method:	std1.1 11;30;40 am-front.mth
Injection Date:	26/2/2010 11:30:40	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2179	2.734	-0.000	10554	0.00	BB	2.6		0
2	Butanetriol(IS1)	11.9895	3.371	0.004	103900	0.00	BB	2.6		0
3	Monoolein	24.8616	12.385	-0.016	215449	0.00	BB	4.5		0
4	Tricaprin(IS2)	53.6904	18.190	0.003	465277	0.00	BB	4.6		0
5	Diolein	4.4390	22.062	-0.001	38468	0.00	BB	4.1		0
6	Trioliein	3.8016	27.768	-0.000	32944	0.00	BB	4.4		0
	Totals	**100.0000**		**-0.010**	**866592**					

Figure A1 GC chromatogram of EN 14105 standard solution 1 (1)

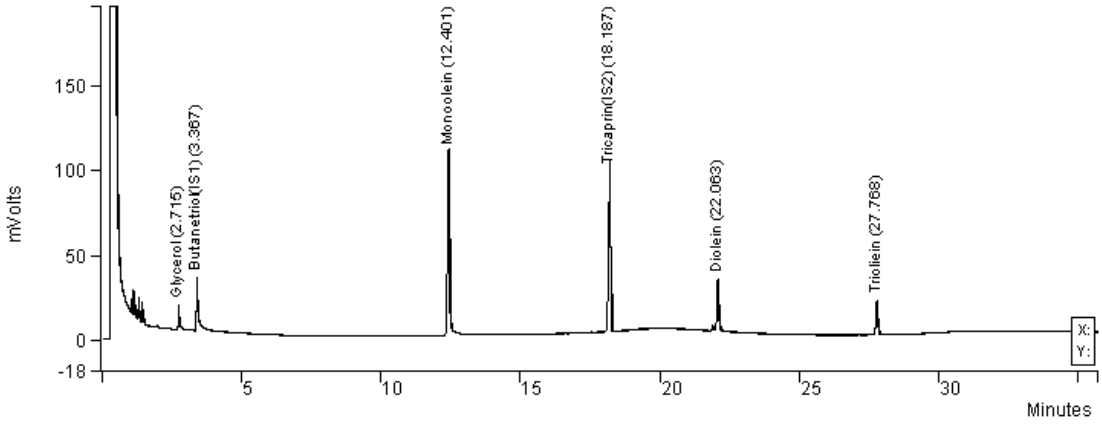
Data File:	c:\star\joe\std1.2 12;21;39 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:36:25
Sample ID:	std1.2	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	std1.1 11;30;40 am-front.mth
Injection Date:	26/2/2010 12:21:39	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	1.2542	2.731	-0.003	11190	0.00	BB	2.5		0
2	Butanetriol(IS1)	12.2305	3.369	0.002	109112	0.00	BB	2.5		0
3	Monoolein	24.8375	12.383	-0.018	221583	0.00	BB	4.4		0
4	Tricaprin(IS2)	53.9499	18.190	0.003	481304	0.00	BB	4.5		0
5	Diolein	4.4034	22.061	-0.002	39284	0.00	BB	4.0		0
6	Trioliein	3.3244	27.763	-0.005	29658	0.00	BB	4.5		0
	Totals	**99.9999**		**-0.023**	**892131**					

Figure A2 GC chromatogram of EN 14105 standard solution 1 (2)

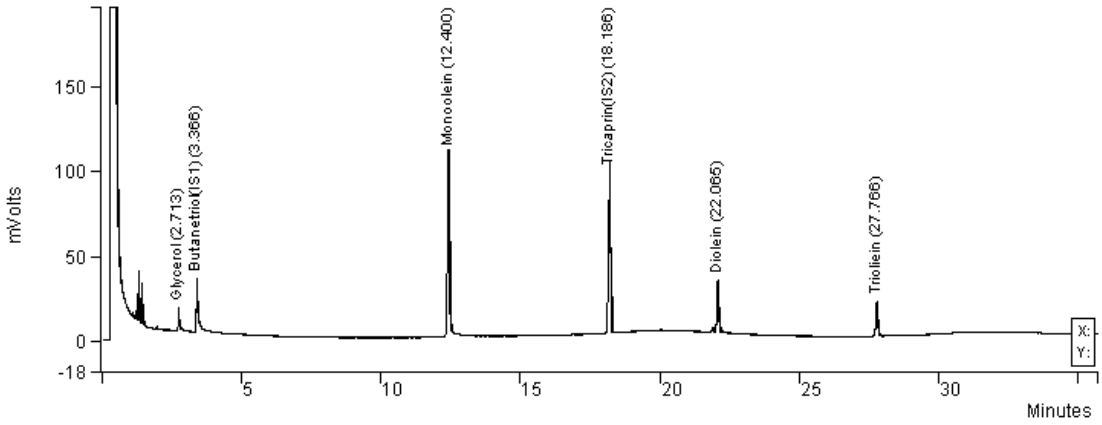
Data File:	c:\star\joe\std2.1 1;12;09 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:29:48
Sample ID:	std2.1	Times Calculated:	5
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 13:12:09	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	2.6591	2.715	-0.020	36824	0.00	BB	2.1		0
2	Butanetriol(IS1)	7.6435	3.367	-0.000	105847	0.00	BB	2.5		0
3	Monoolein	38.1843	12.401	-0.000	528776	0.00	BB	4.3		0
4	Tricaprin(IS2)	35.0148	18.187	-0.000	484885	0.00	BB	4.5		0
5	Diolein	9.6562	22.063	-0.000	133719	0.00	VB	4.1		0
6	Triolein	6.8422	27.768	0.000	94750	0.00	BB	4.4		0
	Totals	**100.0001**		**-0.020**	**1384801**					

Figure A3 GC chromatogram of EN 14105 standard solution 2 (1)

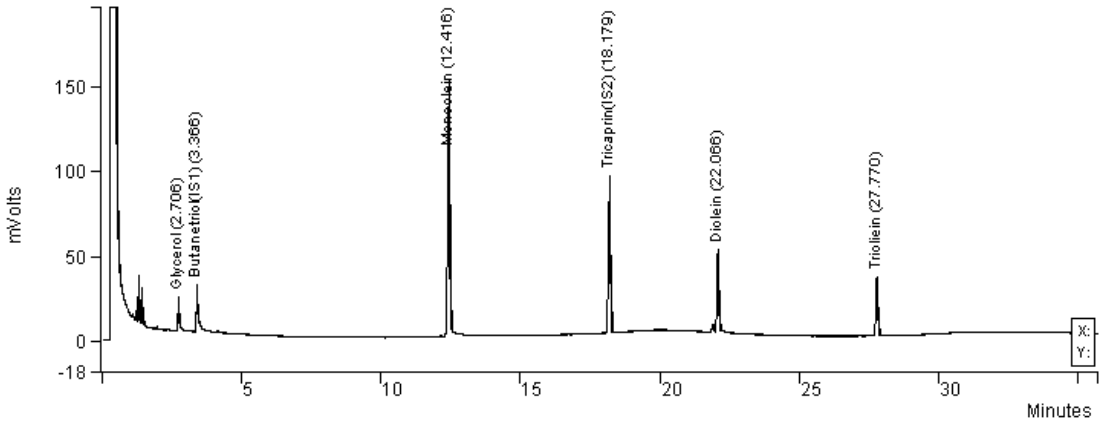
Data File:	c:\star\joe\std2.2 2;02;20 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:28:04
Sample ID:	std2.2	Times Calculated:	3
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 14:02:20	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	2.7003	2.713	-0.002	37959	0.00	BB	2.1		0
2	Butanetriol(IS1)	7.8658	3.366	-0.001	110574	0.00	BB	2.5		0
3	Monoolein	38.1313	12.400	-0.001	536031	0.00	BB	4.4		0
4	Tricaprin(IS2)	34.9182	18.186	-0.001	490864	0.00	BB	4.5		0
5	Diolein	9.6609	22.065	0.002	135809	0.00	VB	4.1		0
6	Triolein	6.7235	27.766	-0.002	94516	0.00	BB	4.4		0
	Totals	**100.0000**		**-0.005**	**1405753**					

Figure A4 GC chromatogram of EN 14105 standard solution 2 (2)

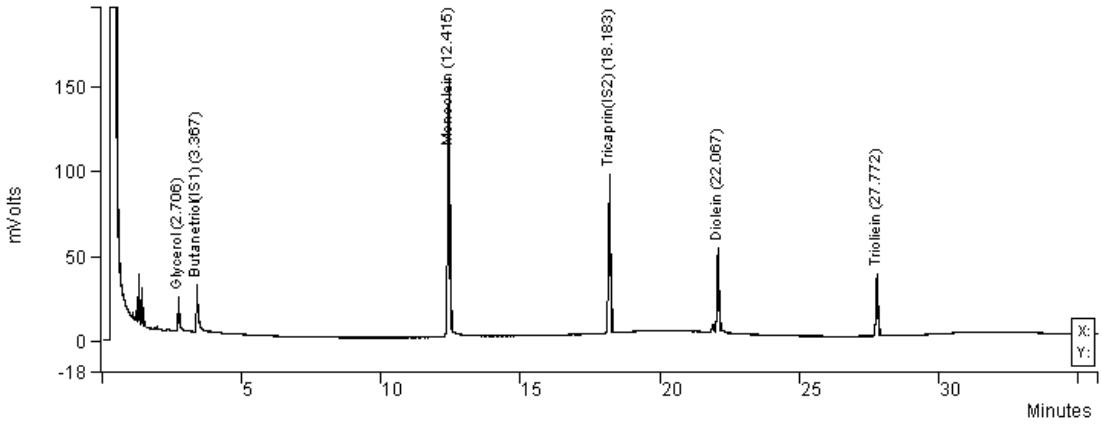
Data File:	c:\star\joe\std3.1 2;52;37 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:28:05
Sample ID:	std3.1	Times Calculated:	3
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 14:52:37	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.2580	2.706	-0.009	56688	0.00	BB	2.4		0
2	Butanetriol(IS1)	5.9095	3.366	-0.001	102822	0.00	BB	2.6		0
3	Monoolein	43.5769	12.416	0.015	758214	0.00	BB	4.6		0
4	Tricaprin(IS2)	25.5245	18.179	-0.008	444111	0.00	BB	4.5		0
5	Diolein	12.1463	22.066	0.003	211338	0.00	VB	4.1		0
6	Trioliein	9.5848	27.770	0.002	166770	0.00	BB	4.4		0
	Totals	**100.0000**		**0.002**	**1739943**					

Figure A5 GC chromatogram of EN 14105 standard solution 3 (1)

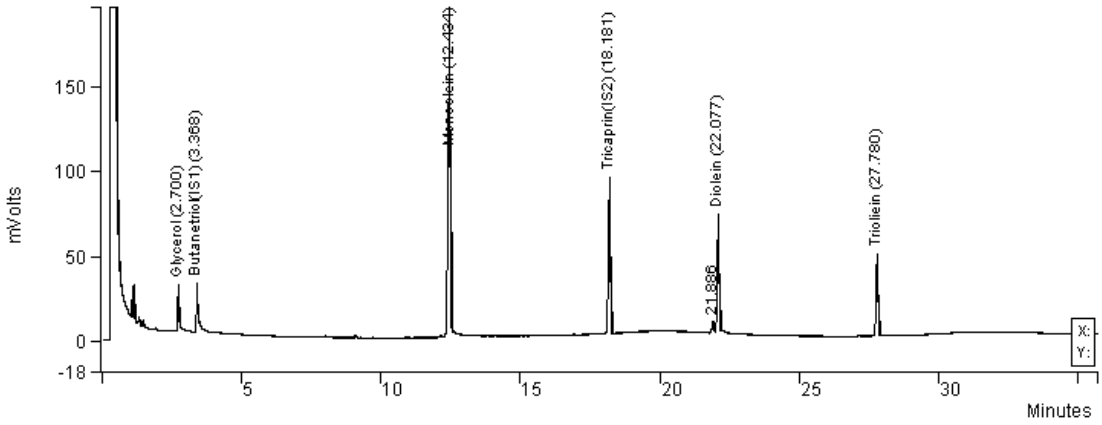
Data File:	c:\star\joe\std3.2 3;42;48 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:29:48
Sample ID:	std3.2	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 15:42:48	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.2183	2.706	-0.029	56811	0.00	BB	2.4		0
2	Butanetriol(IS1)	5.8378	3.367	0.000	103051	0.00	BB	2.6		0
3	Monoolein	43.4559	12.415	0.014	767103	0.00	BB	4.6		0
4	Tricaprin(IS2)	25.4945	18.183	-0.004	450041	0.00	BB	4.5		0
5	Diolein	12.1960	22.067	0.004	215288	0.00	VB	4.1		0
6	Trioliein	9.7975	27.772	0.004	172950	0.00	BB	4.4		0
	Totals	**100.0000**		**-0.011**	**1765244**					

Figure A6 GC chromatogram of EN 14105 standard solution 3 (2)

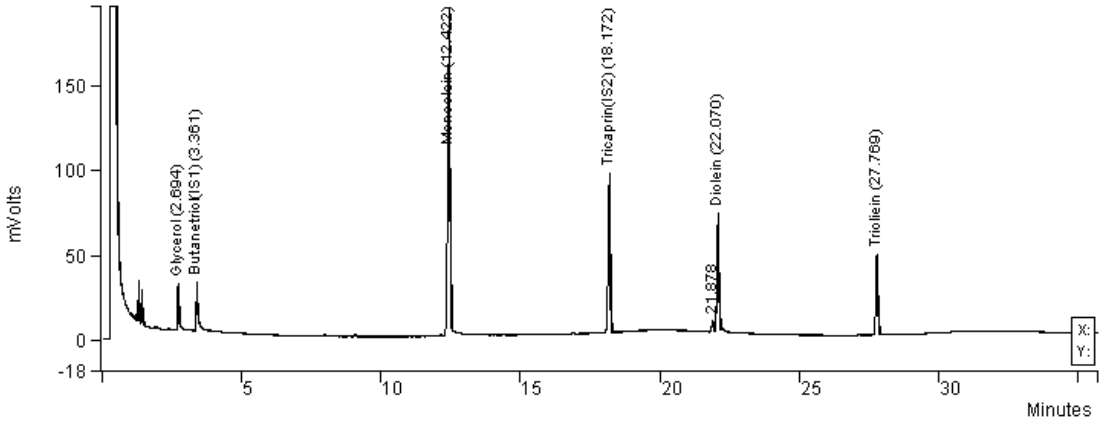
Data File:	c:\star\joe\std4.1 4;38;32 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:29:48
Sample ID:	std4.1	Times Calculated:	5
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 16:38:32	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.5958	2.700	-0.035	79563	0.00	BB	2.5		0
2	Butanetriol(IS1)	4.5792	3.368	0.001	101322	0.00	BB	2.5		0
3	Monoolein	45.8442	12.434	0.033	1014370	0.00	BB	4.9		0
4	Tricaprin(IS2)	20.4509	18.181	-0.006	452505	0.00	BB	4.6		0
5		1.2314	21.886	0.000	27246	0.00	BV	4.2		0
6	Diolein	13.7652	22.077	0.014	304575	0.00	VB	4.2		0
7	Trioliein	10.5332	27.780	0.012	233063	0.00	BB	4.6		0
	Totals	**99.9999**		**0.019**	**2212644**					

Figure A7 GC chromatogram of EN 14105 standard solution 4 (1)

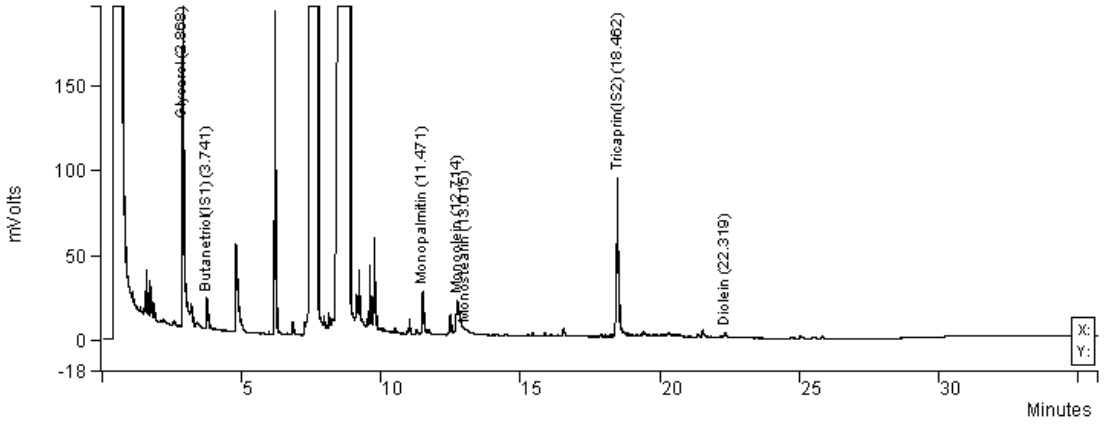
Data File:	c:\star\joe\std4.2 5;29;02 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 17:29:49
Sample ID:	std4.2	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	std2.1 1;12;09 pm-front.mth
Injection Date:	26/2/2010 17:29:02	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	3.6985	2.694	-0.041	81836	0.00	BB	2.5		0
2	Butanetriol(IS1)	4.6654	3.361	-0.006	103228	0.00	BB	2.5		0
3	Monoolein	45.9462	12.422	0.021	1016626	0.00	BB	4.9		0
4	Tricaprin(IS2)	20.4388	18.172	-0.015	452238	0.00	BB	4.5		0
5		1.2199	21.878	0.000	26993	0.00	BV	4.1		0
6	Diolein	13.7870	22.070	0.007	305058	0.00	VB	4.1		0
7	Trioliein	10.2441	27.769	0.001	226666	0.00	BB	4.5		0
	Totals	**99.9999**		**-0.033**	**2212645**					

Figure A8 GC chromatogram of EN 14105 standard solution 4 (2)

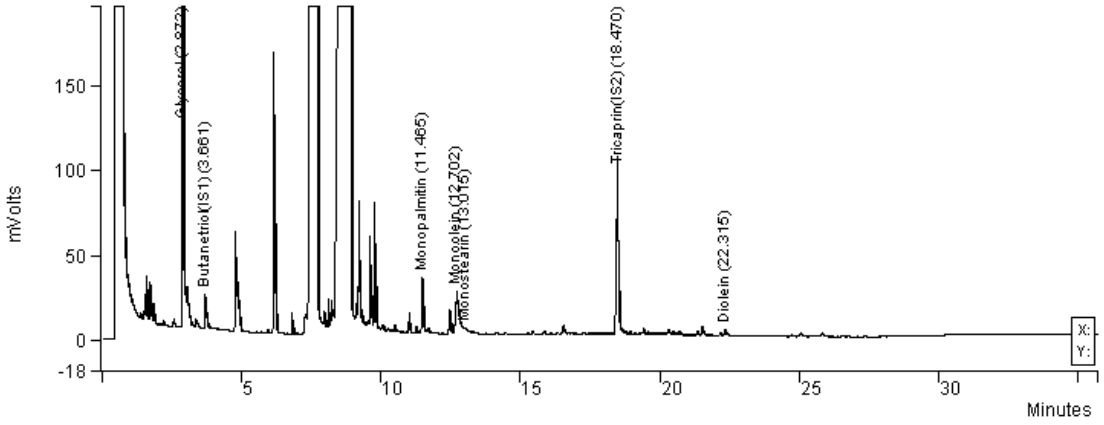
Data File:	c:\star\joe\b_unwash1 4;31;12 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 15:32:13
Sample ID:	b_unwash1	Times Calculated:	4
Operator (Inj):	jo	Calculation Method:	b_unwash1 4;31;12 pm-front.mth
Injection Date:	21/03/2010 16:31:12	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	43.7533	2.868	-0.082	866835	0.00	BB	1.9		0
2	Butanetriol(IS1)	4.2152	3.691	-0.059	83511	0.00	GR	0.0		0
3	Monopalmitin	5.3476	11.471	-0.070	105947	0.00	BV	3.5		0
4	Monoolein	10.5532	12.714	-0.022	209078	0.00	VV	8.1		0
5	Monostearin	1.3941	13.015	-0.078	27620	0.00	VB	5.7		0
6	Tricaprin(IS2)	22.4935	18.462	-0.030	445638	0.00	VP	3.5		0
7	Diolein	0.9415	22.319	-0.005	18653	0.00	GR	0.0		0
	Totals	**88.6984**		**-0.346**	**1757282**					

Figure A9 GC chromatogram of unwashed biodiesel (1)

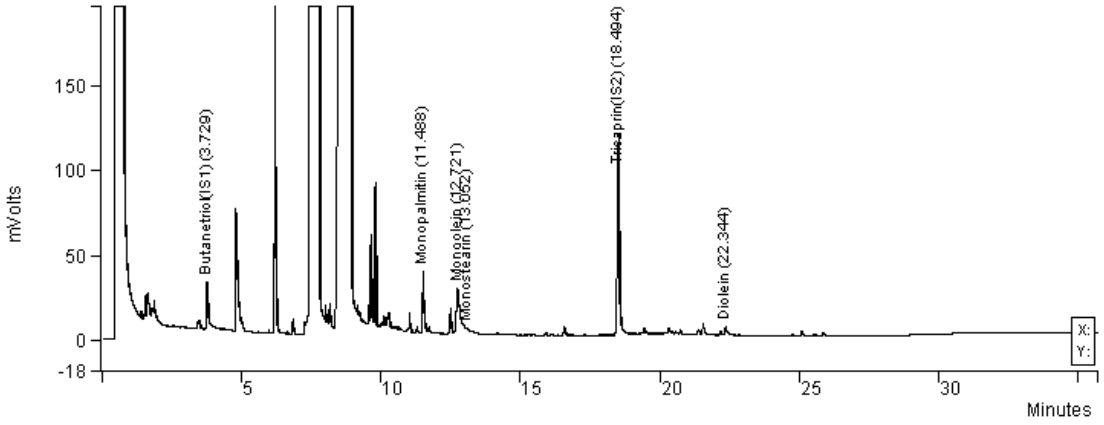
Data File:	c:\star\joe\b_unwash2 5;22;51 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 16:39:34
Sample ID:	b_unwash2	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	b_unwash2 5;22;51 pm-front.mth
Injection Date:	21/03/2010 17:22:51	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	43.0436	2.872	0.022	1006633	0.00	GR	0.0		0
2	Butanetriol(IS1)	4.5588	3.661	0.001	106614	0.00	BB	4.6		0
3	Monopalmitin	5.4635	11.465	-0.076	127772	0.00	BB	3.2		0
4	Monoolein	9.9892	12.702	-0.034	233611	0.00	VV	7.1		0
5	Monostearin	1.3432	13.015	-0.078	31412	0.00	VB	5.6		0
6	Tricaprin(IS2)	22.5466	18.470	-0.022	527283	0.00	PP	4.4		0
7	Diolein	0.8911	22.315	-0.009	20840	0.00	GR	0.0		0
	Totals	**87.8360**		**-0.196**	**2054165**					

Figure A10 GC chromatogram of unwashed biodiesel (2)

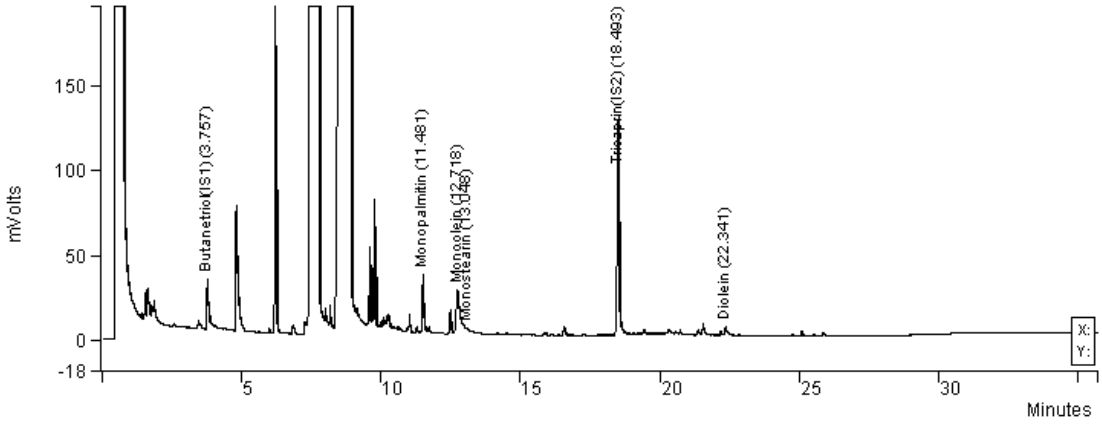
Data File:	c:\star\joe\salt1 10;59;39 am.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 11:59:30
Sample ID:	salt1	Times Calculated:	2
Operator (Inj):	io	Calculation Method:	salt1 10;59;39 am-front.mth
Injection Date:	23/03/2010 10:59:39	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	9.7117	3.729	-0.021	139109	0.00	BB	4.0		0
2	Monopalmitin	9.9557	11.488	-0.053	142605	0.00	BB	3.2		0
3	Monoolein	18.5634	12.721	-0.015	265900	0.00	VV	7.5		0
4	Monostearin	2.5827	13.052	-0.041	36995	0.00	VB	5.5		0
5	Tricaprin(IS2)	41.0439	18.494	0.002	587909	0.00	VP	3.9		0
6	Diolein	1.6124	22.344	0.020	23096	0.00	GR	0.0		0
	Totals	**83.4698**		**-0.108**	**1195614**					

Figure A11 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) (1)

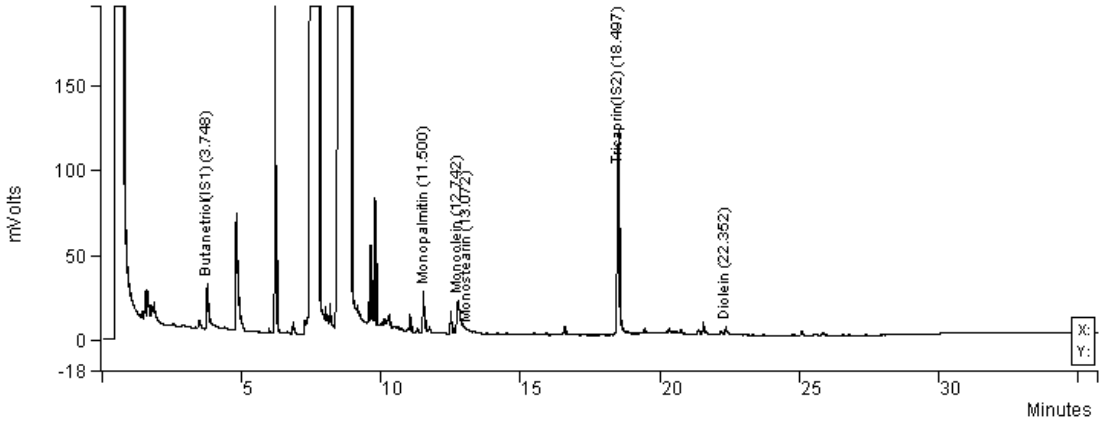
Data File:	c:\star\joe\salt2 11;53;11 am.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 12:12:52
Sample ID:	salt2	Times Calculated:	2
Operator (Inj):	io	Calculation Method:	salt2 11;53;11 am-front.mth
Injection Date:	23/03/2010 11:53:11	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	9.4735	3.757	0.007	130242	0.00	BV	3.6		0
2	Monopalmitin	9.8230	11.481	-0.060	135047	0.00	VV	3.3		0
3	Monoolein	18.9659	12.718	-0.018	260743	0.00	GR	0.0		0
4	Monostearin	2.6024	13.048	-0.045	35778	0.00	VB	0.0		0
5	Tricaprin(IS2)	41.4945	18.493	0.001	570468	0.00	VB	3.3		0
6	Diolein	1.7547	22.341	0.017	24124	0.00	GR	0.0		0
	Totals	**84.1140**		**-0.098**	**1156402**					

Figure A12 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) (2)

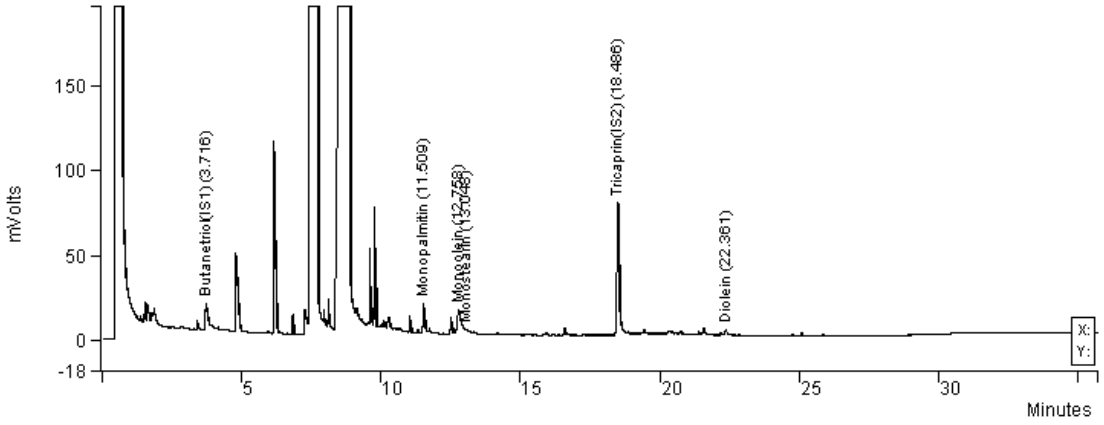
Data File:	c:\star\joe\salt+1%silica1 5;30;51	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 13:06:25
Sample ID:	salt+1%silica1	Times Calculated:	2
Operator (Inj):	io	Calculation Method:	salt+1%silica2 6;21;13 pm-front.mth
Injection Date:	22/03/2010 17:30:51	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.1141	3.748	-0.002	129500	0.00	BV	4.0		0
2	Monopalmitin	7.8407	11.500	-0.041	100392	0.00	VV	3.5		0
3	Monoolein	15.2014	12.742	0.006	194637	0.00	VV	7.9		0
4	Monostearin	1.8665	13.072	-0.021	23899	0.00	VB	5.7		0
5	Tricaprin(IS2)	43.6554	18.497	0.004	558958	0.00	VP	3.5		0
6	Diolein	1.7682	22.352	0.002	22640	0.00	VV	3.8		0
	Totals	**80.4463**		**-0.052**	**1030026**					

Figure A13 GC chromatogram of biodiesel treated with 0.1 % (w/w) silica gel (1)

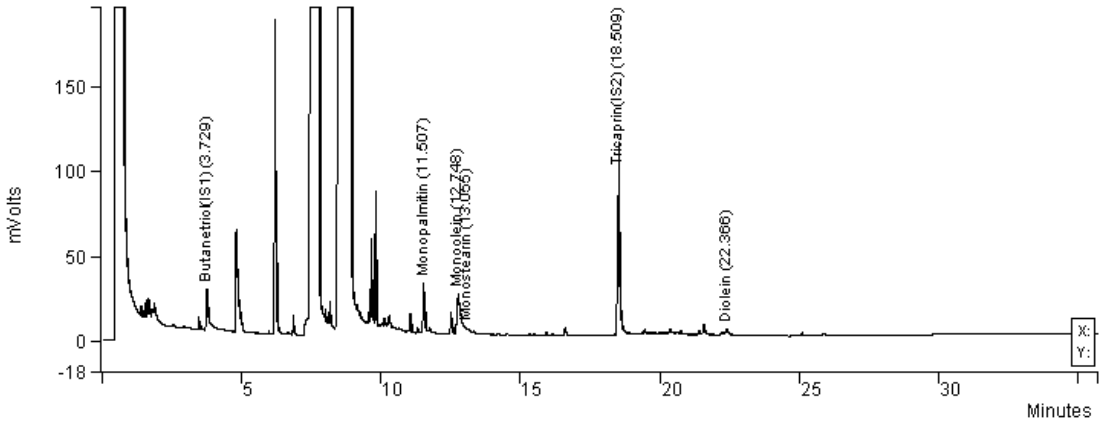
Data File:	c:\star\joe\salt+1%silica2 6;21;13	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 13:19:03
Sample ID:	salt+1%silica2	Times Calculated:	5
Operator (Inj):	io	Calculation Method:	salt+1%silica2 6;21;13 pm-front.mth
Injection Date:	22/03/2010 18:21:13	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	9.8153	3.716	-0.034	94211	0.00	BV	5.6		0
2	Monopalmitin	7.8452	11.509	-0.033	75302	0.00	BV	3.8		0
3	Monoolein	15.4537	12.758	0.022	148331	0.00	VV	8.2		0
4	Monostearin	2.2463	13.048	-0.045	21561	0.00	VB	5.6		0
5	Tricaprin(IS2)	45.5000	18.486	-0.006	436729	0.00	VP	4.6		0
6	Diolein	1.7847	22.361	0.011	17130	0.00	GR	0.0		0
	Totals	**82.6452**		**-0.085**	**793264**					

Figure A14 GC chromatogram of biodiesel treated with 0.1 % (w/w) silica gel (2)

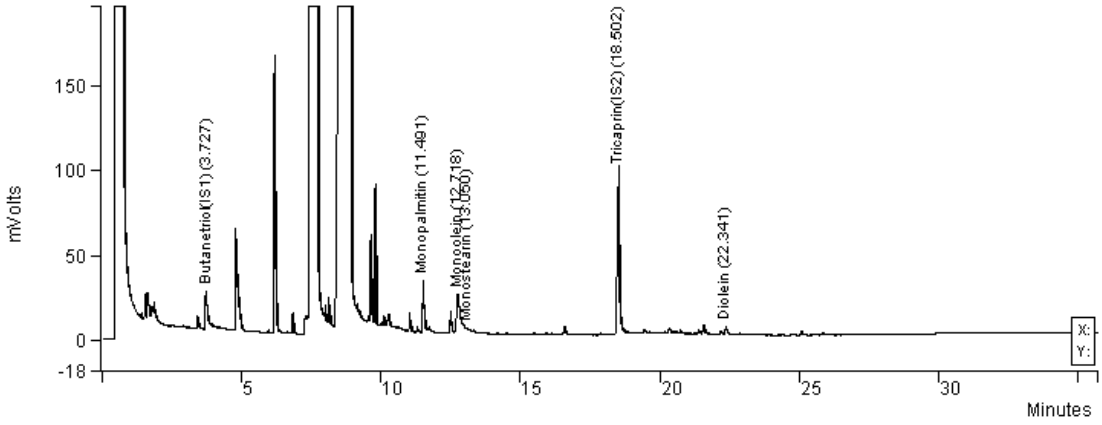
Data File:	c:\star\joe\salt+1%carbon1 2;04;54	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 11:51:38
Sample ID:	salt+1%carbon1	Times Calculated:	2
Operator (Inj):	io	Calculation Method:	salt+1%carbon1 2;04;54 pm-front.mth
Injection Date:	22/03/2010 14:04:54	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.8434	3.729	-0.021	135200	0.00	BB	4.6		0
2	Monopalmitin	9.8132	11.507	-0.034	122356	0.00	BV	3.5		0
3	Monoolein	19.0234	12.748	0.012	237193	0.00	VV	7.6		0
4	Monostearin	2.9971	13.055	-0.038	37369	0.00	VB	5.5		0
5	Tricaprin(IS2)	41.9186	18.509	0.017	522661	0.00	PP	3.4		0
6	Diolein	1.6745	22.366	0.016	20879	0.00	GR	0.0		0
	Totals	**86.2702**		**-0.048**	**1075658**					

Figure A15 GC chromatogram of biodiesel treated with 0.1 %(w/w) activated carbon(1)

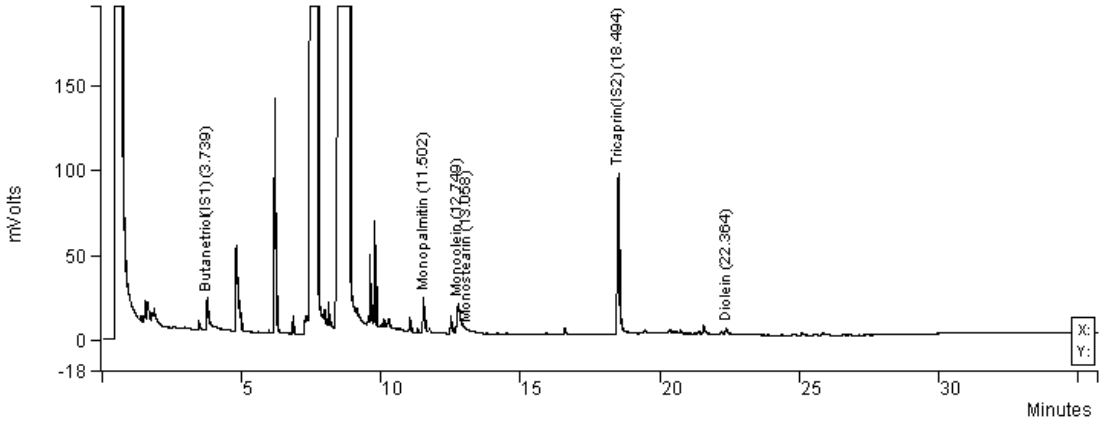
Data File:	c:\star\joe\salt+1%carbon2 2;55;32	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 12:16:35
Sample ID:	salt+1%carbon2	Times Calculated:	2
Operator (Inj):	jo	Calculation Method:	salt+1%carbon2 2;55;32 pm-front.mth
Injection Date:	22/03/2010 14:55:32	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.0697	3.727	-0.023	125196	0.00	GR	0.0		0
2	Monopalmitin	9.0414	11.491	-0.050	112410	0.00	BB	3.4		0
3	Monoolein	18.6431	12.718	-0.018	231788	0.00	GR	0.0		0
4	Monostearin	2.8847	13.050	-0.043	35865	0.00	VB	5.7		0
5	Tricaprin(IS2)	40.3354	18.502	0.010	501487	0.00	VB	4.7		0
6	Diolein	1.7060	22.341	0.017	21210	0.00	GR	0.0		0
	Totals	**82.6803**		**-0.107**	**1027956**					

Figure A16 GC chromatogram of biodiesel treated with 0.1 %(w/w) activated carbon(2)

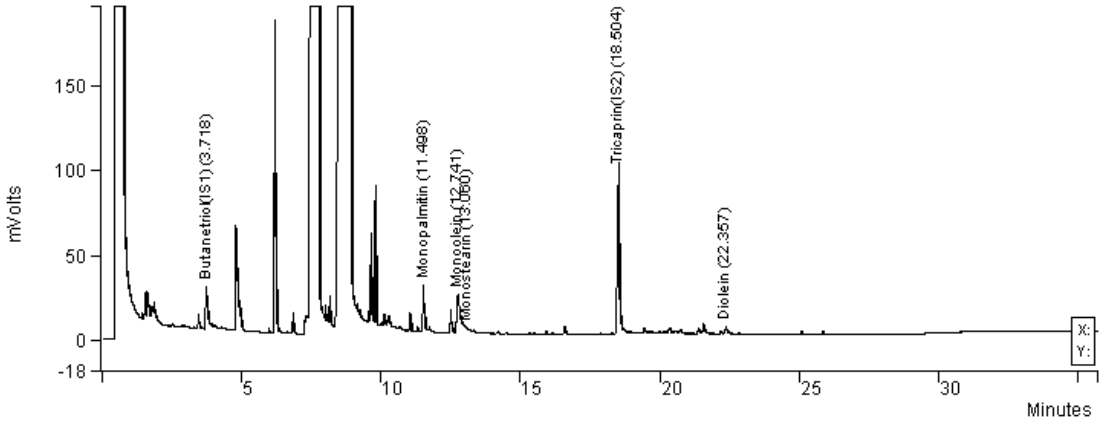
Data File:	c:\star\joe\salt+1%clay1 3;50;07	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 12:26:19
Sample ID:	salt+1%clay1	Times Calculated:	3
Operator (Inj):	io	Calculation Method:	salt+1%clay1 3;50;07 pm-front.mth
Injection Date:	22/03/2010 15:50:07	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	10.5531	3.739	-0.011	112128	0.00	BV	5.0		0
2	Monopalmitin	8.6809	11.502	-0.039	92236	0.00	VV	3.6		0
3	Monoolein	17.1108	12.749	0.013	181805	0.00	VV	8.2		0
4	Monostearin	2.5991	13.058	-0.035	27616	0.00	VB	5.7		0
5	Tricaprin(IS2)	41.0865	18.494	0.002	436550	0.00	PP	3.4		0
6	Diolein	1.5812	22.364	0.040	16800	0.00	VV	4.0		0
	Totals	**81.6116**		**-0.030**	**867135**					

Figure A17 GC chromatogram of biodiesel treated with 0.1 % (w/w) activated clay (1)

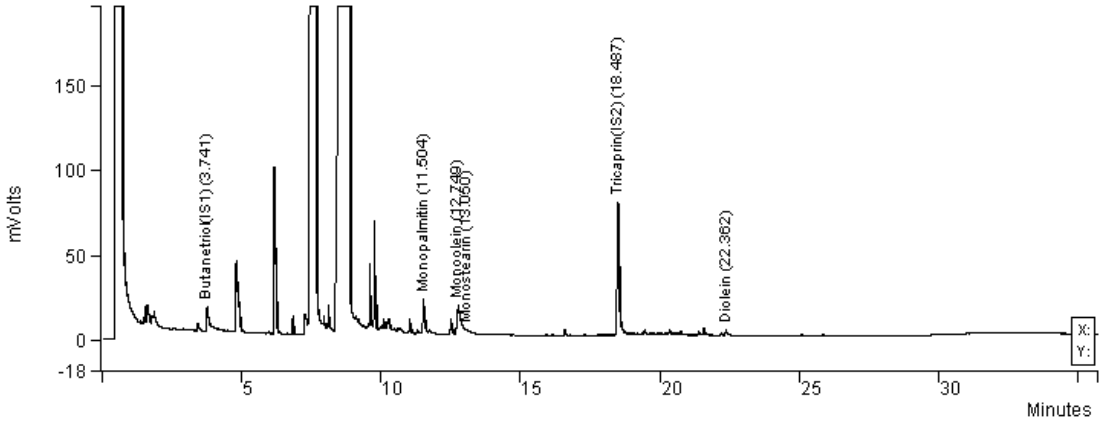
Data File:	c:\star\joe\salt+1%clay2 4;40;34	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	23/03/2010 14:28:34
Sample ID:	salt+1%clay2	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	salt+1%clay2 4;40;34 pm-front.mth
Injection Date:	22/03/2010 16:40:34	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.773	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	9.4166	3.718	-0.032	121416	0.00	BV	4.3		0
2	Monopalmitin	8.5228	11.498	-0.043	109891	0.00	VV	3.3		0
3	Monoolein	17.4642	12.741	0.005	225179	0.00	VV	7.6		0
4	Monostearin	2.4656	13.060	-0.033	31791	0.00	VB	5.7		0
5	Tricaprin(IS2)	41.8801	18.504	0.012	539993	0.00	VP	4.5		0
6	Diolein	1.6286	22.357	0.033	20999	0.00	VV	4.2		0
	Totals	**81.3779**		**-0.058**	**1049269**					

Figure A18 GC chromatogram of biodiesel treated with 0.1 % (w/w) activated clay (2)

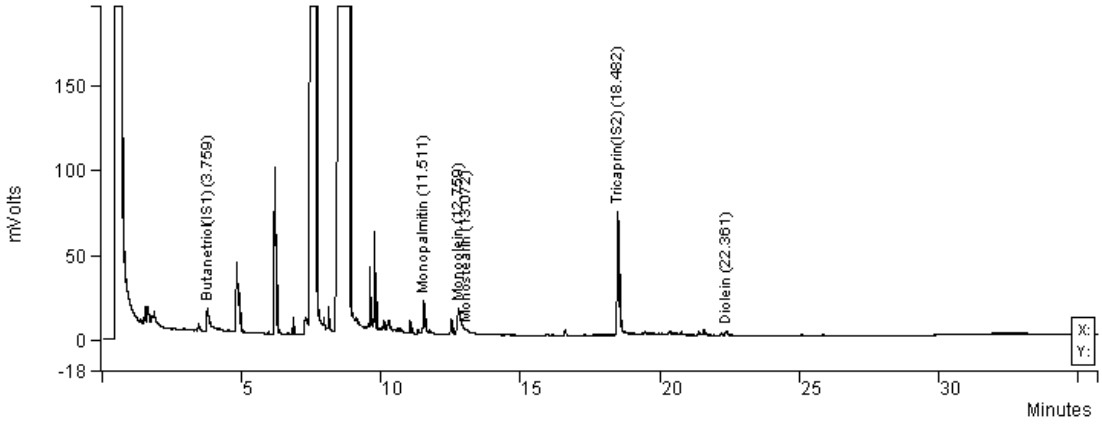
Data File:	c:\star\joe\salt+water1 12;43;04	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 12:52:12
Sample ID:	salt+water1	Times Calculated:	2
Operator (Inj):	io	Calculation Method:	salt+water1 12;43;04 pm-front.mth
Injection Date:	23/03/2010 12:43:04	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	11.1041	3.741	-0.009	105558	0.00	GR	0.0		0
2	Monopalmitin	9.4643	11.504	-0.037	89969	0.00	BV	3.8		0
3	Monoolein	17.8483	12.749	0.013	169669	0.00	VV	7.9		0
4	Monostearin	2.8358	13.050	-0.043	26957	0.00	VB	5.3		0
5	Tricaprin(IS2)	42.1018	18.487	-0.005	400227	0.00	VP	3.7		0
6	Diolein	1.5767	22.362	0.038	14988	0.00	GR	0.0		0
	Totals	**84.9310**		**-0.043**	**807368**					

Figure A19 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) and water (1)

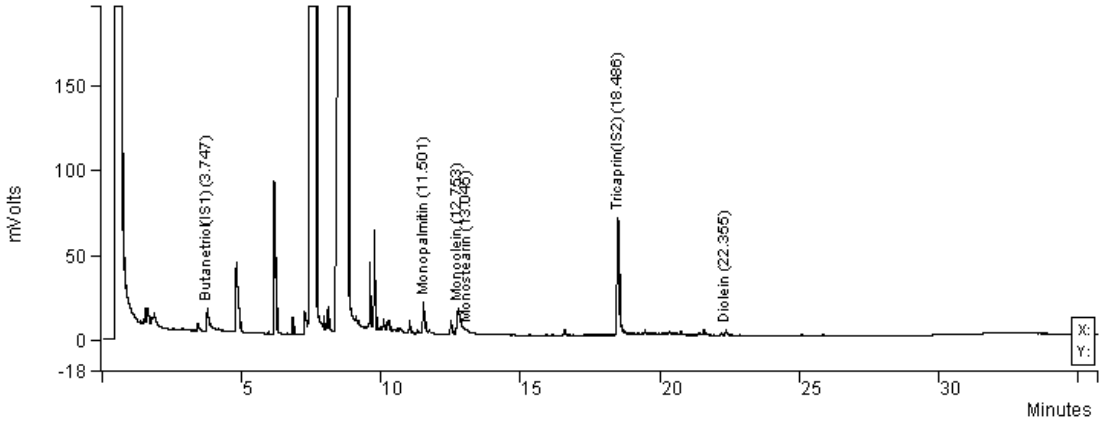
Data File:	c:\star\joe\salt+water2 1;40;44 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 12:36:32
Sample ID:	salt+water2	Times Calculated:	3
Operator (Inj):	io	Calculation Method:	salt+water2 1;40;44 pm-front.mth
Injection Date:	23/03/2010 13:40:44	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	11.3683	3.759	0.009	100918	0.00	BV	5.5		0
2	Monopalmitin	9.4043	11.511	-0.030	83483	0.00	BV	3.7		0
3	Monoolein	17.7751	12.759	0.023	157792	0.00	VV	8.2		0
4	Monostearin	2.3978	13.072	-0.021	21285	0.00	VB	5.5		0
5	Tricaprin(IS2)	42.4896	18.482	-0.010	377186	0.00	VP	3.9		0
6	Diolein	1.5189	22.361	0.011	13483	0.00	VV	4.3		0
	Totals	**84.9540**		**-0.018**	**754147**					

Figure A20 GC chromatogram of biodiesel washed with saturated salt solution (NaCl) and water (2)

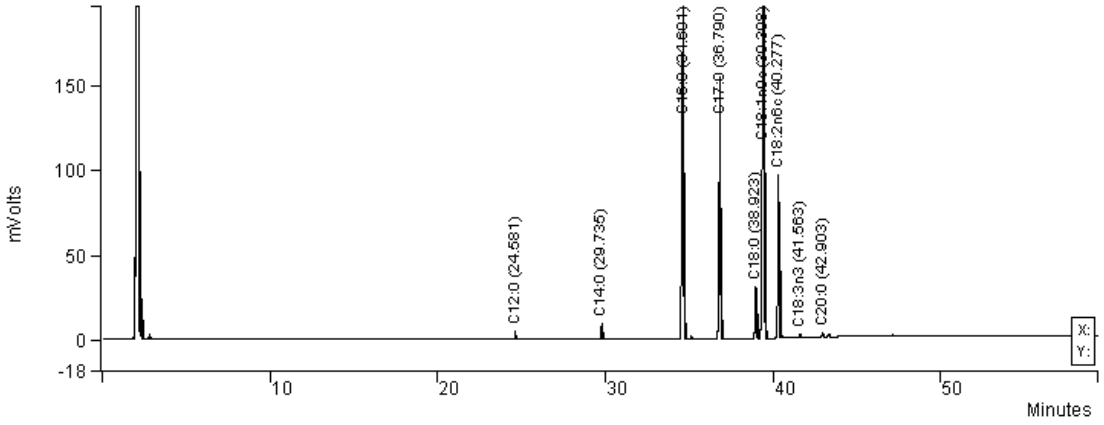
Data File:	c:\star\joe\water 2;31;19 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 15:58:54
Sample ID:	water	Times Calculated:	3
Operator (Inj):	io	Calculation Method:	water 2;31;19 pm-front.mth
Injection Date:	23/03/2010 14:31:19	Instrument (Calc):	gc
Injection Method:	c:\star\en14105.mth	Run Mode:	Analysis
Run Time (min):	35.775	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Butanetriol(IS1)	11.4475	3.747	-0.003	101593	0.00	BV	5.5		0
2	Monopalmitin	9.6626	11.501	-0.040	85752	0.00	VV	3.9		0
3	Monoolein	17.6284	12.753	0.017	156446	0.00	VV	8.0		0
4	Monostearin	2.6362	13.045	-0.048	23395	0.00	VB	5.9		0
5	Tricaprin(IS2)	41.5535	18.486	-0.006	368774	0.00	VP	4.2		0
6	Diolein	1.8888	22.355	0.031	16763	0.00	GR	0.0		0
	Totals	**84.8170**		**-0.049**	**752723**					

Figure A21 GC chromatogram of biodiesel washed with water

Data File:	c:\star\joe\biodiesel 5;09;30 pm.run	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	26/03/2010 10:02:57
Sample ID:	biodiesel	Times Calculated:	4
Operator (Inj):	io	Calculation Method:	biodiesel 5;09;30 pm-front.mth
Injection Date:	18/3/2010 17:09:30	Instrument (Calc):	gc
Injection Method:	c:\labchem07\new method jo-1.2.mth	Run Mode:	Analysis
Run Time (min):	59.440	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C12:0	0.3898	24.581	-0.066	19716	0.00	BB	3.9		0
2	C14:0	0.7837	29.735	-0.070	39639	0.00	BB	4.1		0
3	C16:0	31.6018	34.601	0.048	1598494	0.00	BB	6.1		0
4	C17:0	17.0564	36.790	0.020	862751	0.00	BB	5.2		0
5	C18:0	3.2775	38.923	-0.006	165782	0.00	BB	5.1		0
6	C18:1n9c	36.8763	39.398	0.051	1865288	0.00	BB	6.4		0
7	C18:2n6c	9.5914	40.277	-0.030	485153	0.00	BB	4.7		0
8	C18:3n3	0.1368	41.563	-0.071	6919	0.00	BB	4.1		0
9	C20:0	0.2865	42.903	-0.083	14492	0.00	BB	4.8		0
	Totals	**100.0002**		**-0.207**	**5058234**					

Figure A22 GC chromatogram of fatty acid composition

Appendix B

CALCULATIONS

1. Calculation of soap content

The soap content in the biodiesel was calculated by using the equation:

$$Soap\ content\ (ppm) = \frac{B \times 0.01 \times 303.4}{W \times 1000}$$

Where: B = volume of hydrochloric acid used in second step (mL)

W = weight of untreated biodiesel (g)

Example:

Soap content of biodiesel before washing $= \frac{6.35 \times 0.01 \times 303.4}{4.97 \times 1000}$

= 3539 ppm

Table B1 Soap content of biodiesel washed with three types of saturated salt solution.

Type of salt	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before washing	1	4.97	6.35	3539	3539
	2	5.01	6.40	3539	
NaCl	1	10.02	0.20	28	28
	2	10.00	0.20	28	
KCl	1	10.01	0.10	55	55
	2	10.08	0.10	55	
$Fe_2(SO_4)_3$	1	10.06	ND*	ND	ND
	2	10.05	ND	ND	

***Not detected

Table B2 Soap content of biodiesel washed with saturated salt solution (NaCl) at various shaking time.

Shaking Time	No. of washing	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before washing	-	1	4.99	6.20	3442	3453
		2	5.00	6.25	3463	
30 seconds	1	1	9.95	0.10	28	28
		2	10.12	0.10	27	
	2	1	10.05	0.10	28	28
		2	10.03	0.10	28	
	3	1	9.99	0.05	14	21
		2	10.00	0.10	28	
1 minute	1	1	10.05	0.10	28	28
		2	10.02	0.10	28	
	2	1	10.02	0.10	28	28
		2	10.01	0.10	28	
	3	1	10.02	0.05	14	14
		2	10.04	0.05	14	
3 minutes	1	1	10.01	0.10	28	28
		2	10.05	0.10	28	
	2	1	10.11	0.10	27	21
		2	10.01	0.05	14	
	3	1	10.05	0.05	14	14
		2	10.02	0.05	14	

Table B3 Soap content of biodiesel washed with various ratios of saturated salt solution (NaCl).

Ratio	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before washing	1	5.01	6.00	3317	3317
	2	5.01	6.00	3317	
10:1	1	10.01	0.50	138	132
	2	9.94	0.45	125	
9:1	1	10.00	0.50	139	139
	2	10.00	0.50	139	
8:1	1	10.06	0.45	124	124
	2	10.03	0.45	124	
7:1	1	10.04	0.40	110	110
	2	10.09	0.40	110	
6:1	1	10.05	0.40	110	111
	2	10.00	0.40	111	
5:1	1	10.00	0.30	83	83
	2	10.05	0.30	83	
4:1	1	10.02	0.20	55	55
	2	10.08	0.20	55	
3:1	1	10.02	0.20	55	55
	2	10.04	0.20	55	
2:1	1	10.03	0.20	55	55
	2	10.09	0.20	55	
1:1	1	10.00	0.10	28	28
	2	10.05	0.10	28	
1:2	1	10.00	0.10	28	28
	2	9.96	0.10	28	

Table B4 Soap content of biodiesel washed with saturated salt solution (NaCl) at various temperatures.

Temperature	No. of washing	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before washing	-	1	4.89	6.20	3512	3519
		2	4.91	6.25	3526	
50 ^{o}C	1	1	10.05	0.25	69	69
		2	10.04	0.25	69	
	2	1	10.06	0.30	83	76
		2	10.02	0.25	69	
	3	1	10.00	0.20	55	55
		2	10.01	0.20	55	
Room Temperature	1	1	9.96	0.10	28	28
		2	10.00	0.10	28	
	2	1	10.02	0.10	28	28
		2	10.00	0.10	28	
	3	1	10.00	0.05	14	21
		2	10.12	0.10	27	

Table B5 Soap content of biodiesel washed with saturated salt solution (NaCl) after removed methanol.

Ratio	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Before washing	1	5.02	6.35	3504	3501
	2	5.07	6.40	3497	
Remove methanol	1	10.03	0.60	166	166
	2	10.00	0.60	166	
10:1	1	18.94	0.10	15	15
	2	20.05	0.10	14	
5:1	1	20.12	0.10	14	14
	2	20.01	0.10	14	
1:1	1	19.94	0.05	7	7
	2	20.06	0.05	7	

Table B6 Soap content of biodiesel treated with 0.1 % (w/w) of adsorbents compared with water washing.

Process	Experiment	Weight of sample (g)	Titrant (mL)	Soap content (ppm)	Average
Washing with salt solution	1	10.03	0.10	28	28
	2	10.05	0.10	28	
Salt solution and water	1	10.08	ND*	ND	ND
	2	10.02	ND	ND	
0.1%Silica gel	1	20.05	ND	ND	ND
	2	20.15	ND	ND	
0.1%Activated carbon	1	20.00	ND	ND	ND
	2	20.01	ND	ND	
0.1% Activated clay	1	20.03	ND	ND	ND
	2	20.02	ND	ND	
Water washing	1	20.02	ND	ND	ND
	2	20.05	ND	ND	

*****Not detected

2. Calculation of free and total glycerin calibration functions (Linear regression)

2.1 Free Glycerol

Table B7 Calculation of glycerol calibration function

M_g	M_{is1}	M_g/M_{is1}	A_g	A_{is1}	A_g/A_{is1}
0.005	0.08	0.063	10554	103900	0.102
0.005	0.08	0.063	11190	109112	0.103
0.020	0.08	0.250	36824	105847	0.348
0.020	0.08	0.250	37959	110574	0.343
0.035	0.08	0.438	56688	102822	0.551
0.035	0.08	0.438	56811	103051	0.551
0.050	0.08	0.625	79563	101322	0.785
0.050	0.08	0.625	81836	103228	0.793

Where: M_g is the mass of glycerol (milligrams);

M_{is1} is the mass of IS1 (milligrams);

A_g is the area of glycerol peak.

A_{is1} is the area of IS1 peak.

In regression function X is represented by the term A_g/A_{is1}, while Y is M_g/M_{is1}.

Table B8 Calculation of glycerol calibration function (continued)

X	Y	X^2	Y^2	XY
0.102	0.063	0.010	0.004	0.006
0.103	0.063	0.011	0.004	0.006
0.348	0.250	0.121	0.063	0.087
0.343	0.250	0.119	0.063	0.086
0.551	0.438	0.304	0.191	0.241
0.551	0.438	0.304	0.191	0.241
0.785	0.625	0.617	0.391	0.491
0.793	0.625	0.628	0.391	0.495
ΣX = 3.576	ΣY = 2.750	ΣX^2 = 2.113	ΣY^2 = 1.297	ΣXY = 1.654

$(\Sigma X)^2 = 12.787$ $(\Sigma Y)^2 = 7.563$ N = number of measure = 8

From obtained data can calculate:

$$a_g = \frac{(N \times \Sigma XY) - (\Sigma X \times \Sigma Y)}{(N \times \Sigma X^2) - (\Sigma Y)^2} = \frac{(8 \times 1.654) - (3.576 \times 2.750)}{(8 \times 2.113) - 1.297} = 0.8264$$

$$b_g = \frac{\Sigma Y - (a_g \times \Sigma X)}{N} = \frac{2.750 - (0.8264 \times 3.576)}{8} = -0.0256$$

The correlation coefficient (r) can be calculated from the following equation:

$$r = \frac{(N \times \Sigma XY) - (\Sigma X \times \Sigma Y)}{\sqrt{(N \times \Sigma X^2 - (\Sigma X)^2)\,(N \times \Sigma Y^2 - (\Sigma Y)^2)}}$$

$$= \frac{(8 \times 1.654) - (3.576 \times 2.750)}{\sqrt{(8 \times 2.113 - 12.787)\,(8 \times 1.297 - 7.563)}} = 0.9995$$

2.2 Monoglyceride

Table B9 Calculation of monoglyceride calibration function

M_m	M_{is2}	M_m/M_{is2}	A_m	A_{is2}	A_m/A_{is2}
0.25	0.80	0.313	215449	465277	0.463
0.25	0.80	0.313	221583	481304	0.460
0.60	0.80	0.750	528776	484885	1.091
0.60	0.80	0.750	536031	490864	1.092
0.95	0.80	1.188	758214	444111	1.707
0.95	0.80	1.188	767103	450041	1.705
1.25	0.80	1.563	1014370	452505	2.242
1.25	0.80	1.563	1016626	452238	2.248

Table B10 Calculation of monoglyceride calibration function (continued)

X	Y	X^2	Y^2	XY
0.463	0.313	0.214	0.098	0.145
0.460	0.313	0.212	0.098	0.144
1.091	0.750	1.189	0.563	0.818
1.092	0.750	1.192	0.563	0.819
1.707	1.188	2.915	1.410	2.027
1.705	1.188	2.905	1.410	2.024
2.242	1.563	5.025	2.441	3.503
2.248	1.563	5.053	2.441	3.512
ΣX = 11.007	ΣY = 7.625	ΣX^2 = 18.707	ΣY^2 = 9.023	ΣXY = 12.992

$(\Sigma X)^2 = 121.163$ $(\Sigma Y)^2 = 58.141$ $N = 8$

$$a_m = \frac{(8\times12.992) - (11.007\times7.625)}{(8\times18.707) - 58.141} = 0.7021$$

$$b_m = \frac{7.625 - (0.7021\times11.007)}{8} = -0.1298$$

$$r = \frac{(8\times12.992) - (11.007\times7.625)}{\sqrt{(8\times18.707 - 121.163)\,(8\times9.023 - 58.141)}} = 0.9999$$

2.3 Diglyceride

Table B11 Calculation of diglyceride calibration function

M_d	M_{is2}	M_d/M_{is2}	A_d	A_{is2}	A_d/A_{is2}
0.05	0.80	0.0625	38468	465277	0.083
0.05	0.80	0.0625	39284	481304	0.082
0.20	0.80	0.250	133719	484885	0.276
0.20	0.80	0.250	135809	490864	0.277
0.35	0.80	0.438	211338	444111	0.476
0.35	0.80	0.438	215288	450041	0.478
0.50	0.80	0.625	304575	452505	0.673
0.50	0.80	0.625	305058	452238	0.675

Table B12 Calculation of diglyceride calibration function (continued)

X	Y	X^2	Y^2	XY
0.083	0.063	0.007	0.004	0.005
0.082	0.063	0.007	0.004	0.005
0.276	0.250	0.076	0.063	0.069
0.277	0.250	0.077	0.063	0.069
0.476	0.438	0.226	0.191	0.208
0.478	0.438	0.229	0.191	0.209
0.673	0.625	0.453	0.391	0.421
0.675	0.625	0.455	0.391	0.422
ΣX = 3.019	ΣY = 2.750	ΣX^2 = 1.529	ΣY^2 = 1.297	ΣXY = 1.408

$(\Sigma X)^2 = 9.112$ $(\Sigma Y)^2 = 7.563$ $N = 8$

$$a_d = \frac{(8\times1.408) - (3.019\times2.750)}{(8\times1.529) - 7.563} = 0.9489$$

$$b_d = \frac{2.750 - (0.9489\times3.019)}{8} = -0.1429$$

$$r = \frac{(8\times1.408) - (3.019\times2.750)}{\sqrt{(8\times1.529 - 9.112)\,(8\times1.297 - 7.563)}} = 0.9999$$

2.4 Triglyceride

Table B13 Calculation of triglyceride calibration function

M_t	M_{is2}	M_t/M_{is2}	A_t	A_{is2}	A_t/A_{is2}
0.05	0.80	0.063	32944	465277	0.071
0.05	0.80	0.063	29658	481304	0.062
0.15	0.80	0.188	94750	484885	0.195
0.15	0.80	0.188	94516	490864	0.193
0.30	0.80	0.375	166770	444111	0.376
0.30	0.80	0.375	172950	450041	0.384
0.40	0.80	0.500	233063	452505	0.515
0.40	0.80	0.500	226666	452238	0.501

Table B14 Calculation of triglyceride calibration function (continue)

X	Y	X^2	Y^2	XY
0.071	0.063	0.005013	0.004	0.004
0.062	0.063	0.003797	0.004	0.004
0.195	0.188	0.038184	0.035	0.037
0.193	0.188	0.037076	0.035	0.036
0.376	0.375	0.141011	0.141	0.141
0.384	0.375	0.147685	0.141	0.144
0.515	0.500	0.265277	0.250	0.258
0.501	0.500	0.251211	0.250	0.251
ΣX = 2.296	ΣY = 2.250	ΣX^2 = 0.889	ΣY^2 = 0.859	ΣXY = 0.874

$(\Sigma X)^2 = 5.274$ $(\Sigma Y)^2 = 5.063$ $N = 8$

$$a_t = \frac{(8\times 0.874) - (2.296\times 2.250)}{(8\times 0.889) - 5.063} = 0.9920$$

$$b_t = \frac{2.250 - (0.9920\times 2.296)}{8} = -0.0035$$

$$r = \frac{(8\times 0.874) - (2.296\times 2.250)}{\sqrt{(8\times 0.889 - 5.274)\,(8\times 0.859 - 5.063)}} = 0.9996$$

3. Calculation of the percentage of free and total glycerin

The percentage (*m/m*) of free glycerol in the sample was calculated by the following equation:

$$G = [a_g\ (A_g / A_{eil}) + b_g] \times (M_{eil}\ /m) \times 100$$

Where: G = percentage (*m/m*) of free glycerol

A_g = peak area of the glycerol

A_{eil} = peak area of internal standard No. 1

M_{eil} = mass of internal standard No. 1 (milligrams)

m = mass of sample (milligrams)

a_g and b_g = constants coming from regression method for glycerol

The percentage (*m/m*) of mono-, di- and triglycerides in the sample were calculated by the following equation:

$$M = [a_m\ (\Sigma A_{mi}/A_{ei2}) + b_m] \text{ x } (M_{ei2}/m) \times 100$$
$$D = [a_d\ (\Sigma A_{di}/A_{ei2}) + b_d] \times (M_{ei2}/m) \times 100$$
$$T = [a_t\ (\Sigma A_{ti}/A_{\ ei2}) + b_t] \times (M_{ei2}/m) \times 100$$

Where: M, D, T = percentage (*m/m*) of mono-, di- and triglyceride

$\Sigma A_{mi}, \Sigma A_{di}, \Sigma A_{ti}$ = sums of the peak areas of the mono-, di- and triglycerides

A_{ei2} = peak area of internal standard No 2

M_{ei2} = mass of internal standard No 2 (milligrams)

m = mass of sample (milligrams)

a_m and b_m = constants coming from regression method for monoglyceride

a_d and b_d = constants coming from regression method for diglyceride

a_t and b_t = constants coming from regression method for triglyceride

The percentage (*m/m*) of total glycerin in the sample was calculated by the following equation:

$$GT = G + 0.255\,M + 0.146\,D + 0.103\,T$$

Where: *G*T = percentage (*m/m*) of total glycerin (free and bound)
G = percentage (*m/m*) of free glycerol in the sample
M = percentage (*m/m*) of monoglycerides in the sample
D = percentage (*m/m*) of diglycerides in the sample
T = percentage (*m/m*) of triglycerides in the sample

Table B15 The percentage of free glycerol (%wt) of biodiesel

Samples		Peak area (Sample)	Peak area (IS1)	Weight of sample (mg)	%Free	Average	STDEV
Unwashed biodiesel	1	866835	83511	100.0	0.684	0.653	0.0438
	2	1006633	106614	100.0	0.622		
Washing with salt solution	1	ND*	139109	100.0	ND	ND	-
	2	ND	130242	100.0	ND		
Salt solution and water	1	ND	105558	100.0	ND	ND	-
	2	ND	100918	100.0	ND		
0.1% Silica gel	1	ND	129500	100.1	ND	ND	-
	2	ND	94211	100.1	ND		
0.1%Activated carbon	1	ND	135200	100.1	ND	ND	-
	2	ND	125196	100.1	ND		
0.1% Activated clay	1	ND	112128	100.0	ND	ND	-
	2	ND	121416	100.0	ND		
Water washing		ND	101593	100.0	ND	ND	-

*Not detected

Table B16 The percentage of monoglyceride (%wt) of biodiesel

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Mono	Average	STDEV
Unwashed biodiesel	1	342645	445638	100.0	0.422	0.415	0.00990
	2	392795	527283	100.0	0.408		
Washing with salt solution	1	445500	587909	100.0	0.415	0.415	0
	2	431568	570468	100.0	0.415		
Salt solution and water	1	286595	400227	100.0	0.392	0.387	0.00778
	2	262560	377186	100.0	0.381		
0.1% Silica gel	1	318928	558958	100.1	0.310	0.308	0.00354
	2	245174	436729	100.1	0.305		
0.1%Activated carbon	1	396918	522661	100.1	0.416	0.416	0.00071
	2	380063	501487	100.1	0.415		
0.1% Activated clay	1	301657	436550	100.0	0.378	0.375	0.00495
	2	366861	539993	100.0	0.371		
Water washing		265593	368774	100.0	0.394	0.394	-

Table B17 The percentage of diglyceride (%wt) of biodiesel

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Di	Average	STDEV
Unwashed biodiesel	1	18653	445638	100.0	0.0321	0.0311	0.00148
	2	20840	527283	100.0	0.0300		
Washing with salt solution	1	23096	587909	100.0	0.0298	0.0312	0.00191
	2	24124	570468	100.0	0.0325		
Salt solution and water		14988	400227	100.0	0.0281	0.0273	0.00113
		13483	377186	100.0	0.0265		
0.1% Silica gel	1	22640	558958	100.1	0.0308	0.0303	0.00078
	2	17130	436729	100.1	0.0297		
0.1%Activated carbon	1	20879	522661	100.1	0.0303	0.0314	0.00156
	2	21210	501487	100.1	0.0325		
0.1% Activated clay	1	16800	436550	100.0	0.0290	0.0292	0.00028
	2	20999	539993	100.0	0.0294		
Water washing		16763	368774	100.0	0.0280	0.0280	-

Table B18 The percentage of triglyceride (%wt) of biodiesel

Samples		Peak area (Sample)	Peak area (IS2)	Weight of sample (mg)	%Tri	Average	STDEV
Unwashed biodiesel	1	-*	445638	100.0	-	-	-
	2	-	527283	100.0	-		
Washing with salt solution	1	-	587909	100.0	-	-	-
	2	-	570468	100.0	-		
Salt solution and water	1	-	400227	100.0	-	-	-
	2	-	377186	100.0	-		
0.1% Silica gel	1	-	558958	100.1	-	-	-
	2	-	436729	100.1	-		
0.1%Activated carbon	1	-	522661	100.1	-	-	-
	2	-	501487	100.1	-		
0.1% Activated clay	1	-	436550	100.0	-	-	-
	2	-	539993	100.0	-		
Water washing		-	368774	100.0	-	-	-

*Data not available

Table B19 The percentage of total glycerin (%wt) of biodiesel

Samples		Free glycerol	Mono	Di	Tri	Total glycerin	Average	STDEV
Unwashed biodiesel	1	0.684	0.422	0.0321	-	0.796	0.763	0.0467
	2	0.622	0.408	0.0300	-	0.730		
Washing with salt solution	1	ND	0.415	0.0298	-	0.110	0.111	0.00071
	2	ND	0.415	0.0325	-	0.111		
Salt solution and water	1	ND	0.392	0.0281	-	0.104	0.0103	0.00212
	2	ND	0.381	0.0265	-	0.101		
0.1% Silica gel	1	ND	0.310	0.0308	-	0.0835	0.0828	0.00099
	2	ND	0.305	0.0297	-	0.0821		
0.1% Activated carbon	1	ND	0.416	0.0303	-	0.111	0.111	0
	2	ND	0.415	0.0325	-	0.111		
0.1% Activated clay	1	ND	0.378	0.0290	-	0.101	0.100	0.00149
	2	ND	0.371	0.0294	-	0.0989		
Water washing		ND	0.394	0.0280	-	0.105	0.105	-

4. Determination of sodium content

Sodium content was determined by using AAnalyst 100, Perkin Elmer atomic absorption spectrometer. The standard curve of sodium ion was plotted between intensity and concentration using the concentrations of sodium standard solution at 0.1, 0.5, 1, 3 and 5 ppm.

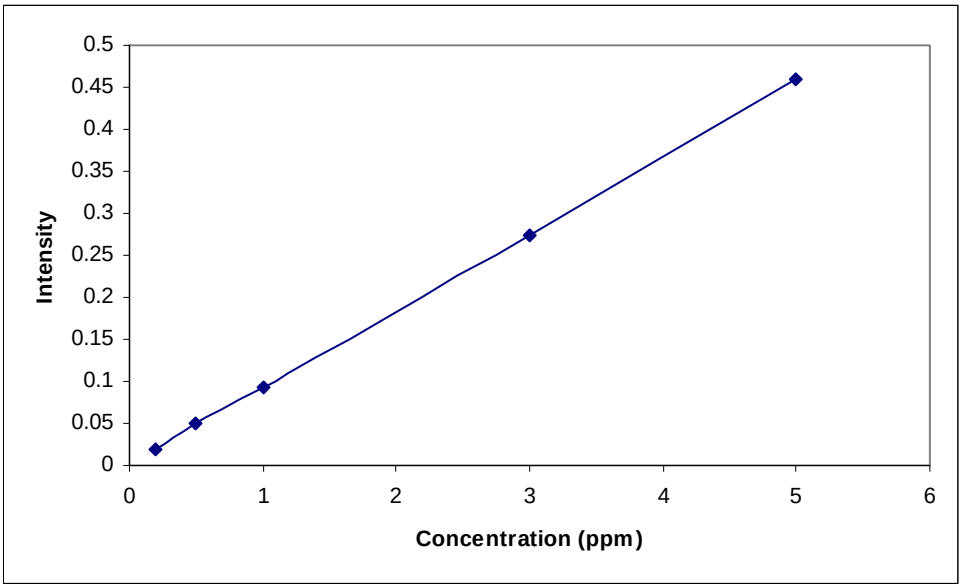


Figure B1 The standard curve of sodium standard solution

Wavelength of Na lamp = 599.0 nm

R^2 = 0.99998

4. Determination of the acid value (ASTM D974)

Reagent

1. p-naphtholbenzein indicator solution

2. 0.1 M Alcoholic KOH solution (0.6 g of potassium hydroxide was dissolved in 100 ml of isopropyl alcohol)

3. Titration solvent (Mixture of 250 ml of toluene and 250 ml of isopropyl alcohol)

2 g of oil sample, 25 ml of titration solvent and 0.125 ml of 1% p-naphtholbenzein indicator solution were added into the 250 ml of Erlenmeyer flask. The mixture was subject to titrate with 0.1 M of alcoholic KOH until the green color was occurred. A blank determination was prepared and carried out same with the sample. The ml of acid solution used was recorded. The acid value was calculated by using the equation:

$$Acid\ value = \frac{(A-B) \times M \times 56.1}{weight\ of\ sample}$$

Where: A = titration of sample

B = titration of blank

M = concentration of alcoholic KOH

Example:

Acid value of biodiesel washed with $Fe_2(SO_4)_3$ solution

$$= \frac{(0.250-0.025) \times 0.0961 \times 56.1}{2.0110}$$

= 0.603 mg KOH/g of oil

Table B20 Acid value of biodiesel

Process	Weight of sample (g)	Titrant (mL)	Blank (mL)	Acid value	Average
Washing with salt solution	2.0145	0.025	0.025	0	0
	2.0101	0.025	0.025	0	
Salt solution and water	2.0230	0.050	0.025	0.067	0.067
	2.0332	0.050	0.025	0.066	
0.1% Silica gel	2.0035	0.050	0.025	0.067	0.067
	2.0068	0.050	0.025	0.067	
0.1% Activated carbon	2.0111	0.050	0.025	0.067	0.067
	2.0359	0.050	0.025	0.066	
0.1% Activated clay	2.0403	0.050	0.025	0.066	0.066
	2.0254	0.050	0.025	0.066	
Water washing	2.0395	0.050	0.025	0.066	0.067
	2.0108	0.050	0.025	0.067	

5. Determination of viscosity (ASTM D445)

7 ml of each sample was added into the Viscometer tube and the viscometer was inserted into the bath. After insertion, the viscometer was allowed to reach bath temperature. The suction was used to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark. The sample was measured with the flowing freely in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. The time of sample used was recorded. The viscosity was calculated by using the equation:

$$Viscosity = Ct$$

Where: C = Constant of viscometer tube (constant values of no.150 of viscometer tube = 0.0337 mm^2/s^2)

t = measured flow times for *t1* and *t2*, respectively(s)

Example:

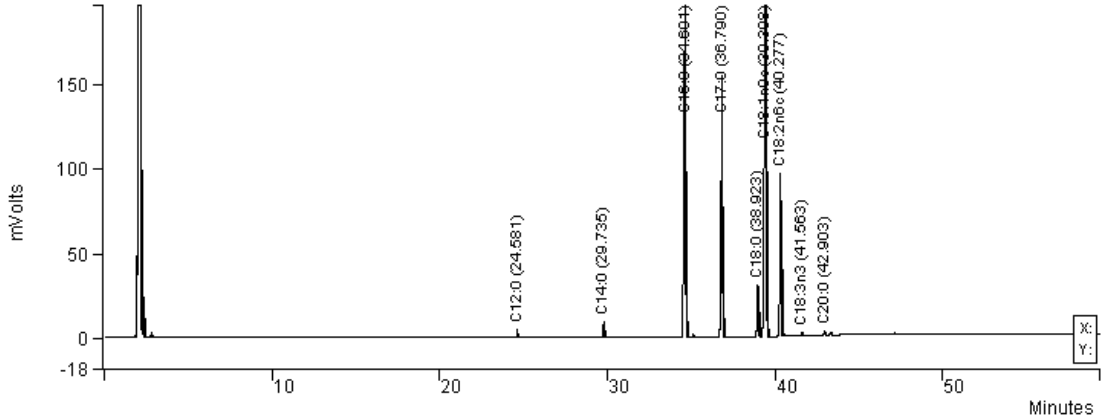
$$\text{Viscosity of biodiesel washed with water} = 0.0337 \times \frac{(124.24+124.18)}{2}$$

$$= 4.2\ mm^2/s$$

Table B21 Viscosity of biodiesel

Process	Time1 (s)	Time2 (s)	Constant value of tube	Viscosity (mm^2/s)
Washing with salt solution	129.55	129.39	0.0337	4.4
Salt solution and water	124.24	124.18	0.0337	4.2
0.1% Silica gel	124.54	124.46	0.0337	4.2
0.1% Activated carbon	123.95	123.81	0.0337	4.2
0.1%Activated clay	125.16	124.88	0.0337	4.2
Water washing	124.09	124.23	0.0337	4.2

6. Calculation of %Methyl ester content from GC



Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C12:0	0.3898	24.581	-0.066	19716	0.00	BB	3.9		0
2	C14:0	0.7837	29.735	-0.070	39639	0.00	BB	4.1		0
3	C16:0	31.6018	34.601	0.048	1598494	0.00	BB	6.1		0
4	C17:0	17.0564	36.790	0.020	862751	0.00	BB	5.2		0
5	C18:0	3.2775	38.923	-0.006	165782	0.00	BB	5.1		0
6	C18:1n9c	36.8763	39.398	0.051	1865288	0.00	BB	6.4		0
7	C18:2n6c	9.5914	40.277	-0.030	485153	0.00	BB	4.7		0
8	C18:3n3	0.1368	41.563	-0.071	6919	0.00	BB	4.1		0
9	C20:0	0.2865	42.903	-0.083	14492	0.00	BB	4.8		0
	Totals	**100.0002**		**-0.207**	**5058234**					

%Methyl ester content from GC of biodiesel can be calculated by the following equation:

$$C = \frac{(\Sigma A - A_i)}{A_i} \times \frac{(C_i \times V_i)}{m} \times 100$$

Where: C = Methyl ester content

ΣA = Total area of fatty acid methyl esters

A_i = Area of methyl heptadecanoate

C_i = Concentration of methyl heptadecanoate solution

V_i = Volume of methyl heptadecanoate solution

m = Mass of the sample (mg)

$$C = \frac{(5058234 - 862751)}{862751} \times \frac{(10.0224 \times 5)}{257.16} \times 100$$

$$= 94.76\ \%$$

VITA

Mr. Methawaj Rungsiriworapong was born on March 9, 1984 in Bangkok, Thailand. He graduated at Triam Udomsuksa Pattanakarn School in 2002. He received the Bachelor Degree of Science in chemistry, Chulalongkorn University in 2006. He continued his Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkom University in 2006 and completed the program in 2010.

Conference

21-23 January 2010 “Purification of biodiesel using adsorbents and saturated salt solution”
Pure and Applied Chemistry International Conference 2010
UBON RATCHATHANI UNIVERSITY