การทำไบโอดีเซลให้บริสุทธิ์โดยใช้โดยใช้ดินเบาและผิวดินเบาเคลือบแมงกานีสออกไซด์

นางสาวนิสากรณ์ แสงประชุม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

PURIFICATION OF BIODIESEL USING NATURAL DIATOMITE AND DIATOMITE DOPED WITH MnO_2

Miss Nisakorn Saengprachum

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Enivironmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2009

Thesis Title PURIFICATION OF BIODIESEL USING NATURAL DIATOMITE AND DIATOMITE DOPED WITH MnO_2
By Miss Nisakorn Saengprachum
Field of Study Environmental Management
Thesis Advisor Associate Professor Somchai Pengprecha, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………….. Dean of the Graduate School
(Associate Professor Pornpote Piumsomboon, Ph.D.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Assistant Professor Manaskorn Rachakornkij, Ph.D.)

……………………………………………….. Thesis Advisor
(Associate Professor Somchai Pengprecha, Ph.D.)

……………………………………………….. Examiner
(Chantra Tongcumpou, Ph.D.)

……………………………………………….. Examiner
(Nyein Nyein Aung, Ph.D.)

……………………………………………….. External Examiner
(Kunn Kangwansaichol, Ph.D.)

นิสากรณ์ แสงประชุม: การทำไบโอดีเซลให้บริสุทธิ์โดยใช้โดยใช้ดินเบาและผิวดินเบาเคลือบแมงกานีสออกไซด์. (PURIFICATION OF BIODIESEL USING NATURAL DIATOMITE AND DIATOMITE DOPED WITH MnO_2) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รองศาสตราจารย์ ดร. สมใจ เพ็งปรีชา, 138 หน้า.

งานวิจัยนี้มีจุดประสงค์คือเพื่อศึกษา การทำไบโอดีเซลให้บริสุทธิ์ด้วยกระบวนการดูดซับโดยใช้ดินเบา และ ดินเบาเคลือบแมงกานีสออกไซด์เป็นตัวดูดซับ

ในการศึกษานี้ใช้ดินเบาเพื่อกำจัดกลีเซอรีนออกจากไบโอดีเซล จากนั้นเพิ่มความสามารถในการดูดซับของดินเบาด้วยการเคลือบแมงกานีสอออกไซด์ 0.118 กรัมต่อดินเบา 1 กรัม ซึ่งดินเบาเคลือบแมงกานีสออกไซด์นี้ใช้ในการกำจัดโมโนกลีเซอไรด์ออกจากไบโอดีเซล พื้นที่ผิวของดินเบาและดินเบาเคลือบแมงกานีสออกไซด์ซึ่งคำนวณจากเทคนิค BET มีค่าเท่ากับ 66 และ 138 ตารางเมตรต่อกรัมตามลำดับ จากการศึกษาพบว่าประสิทธิภาพเหมาะที่สุดในการกำจัดกลีเซอรีนสามารถได้จากการใช้ดินเบาร้อยละ 4 โดยน้ำหนัก เวลาในการสัมผัส 20 นาที ที่ 50 องศาเซลเซียส นอกจากนี้โดยการกำจัดเมทานอลออกจากไบโอดีเซลก่อนทำการดูดซับสามารถกำจัดกลีเซอรีนได้ร้อยละ 98 โดยใช้ดินเบาร้อยละ 1 โดยน้ำหนัก ที่สภาวะเดียวกัน และสามารถกำจัดโมโนกลีเซอไรด์ได้ร้อยละ 28.92 โดยการใช้ดินเบาเคลือบแมงกานีสออกไซด์ร้อยละ 2 โดยน้ำหนัก เวลาในการสัมผัส 10 นาที ที่ 50 องศาเซลเซียส จากการศึกษาไอโซเทอมการดูดซับของกลีเซอรีนและโมโนกลีเซอไรด์พบว่าสอดคล้องกับไอโซเทอมการดูดซับแบบฟรุนดิกและแลงเมียร์ กระบวนการนี้ให้คุณภาพของไบโอดีเซลเทียบเท่ากับกระบวนการล้างด้วยน้ำ และให้ค่าความเป็นกรด ความหนืด จุดวาบไฟ และกลีเซอรีนอิสระและกลีเซอรีนทั้งหมดผ่านเกณฑ์มาตรฐานของไบโอดีเซล ข้อดีของกระบวนการนี้เหนือกระบวนการล้างด้วยน้ำคือไม่มีน้ำเสียเกิดขึ้น

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต
ปีการศึกษา 2552 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

5187541020 : MAJOR ENVIRONMENTAL MANAGEMENT

KEYWORDS: DIATOMITE/ DRY-WASHING PROCESS/ MODIFIED DIATOMITE/ ADSORPTION

NISAKORN SAENGPRACHUM: PURIFICATION OF BIODIESEL USING NATURAL DIATOMITE AND DIATOMITE DOPED WITH MnO_2. THESIS ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 138 pp.

This research aims to study an adsorption process for purifying biodiesel by using natural diatomite (D) and MnO_2-doped diatomite (DDM) as adsorbents.

Natural diatomite was firstly used for removal of glycerin from crude biodiesel. The sorption capacity of natural diatomite was further improved by doping diatomite with 0.118 g of manganese oxide per g diatomite, and used for removal of monoglyceride. The surface area of diatomite and MnO_2-doped diatomite calculated using BET method were 66 and 138 m^2g^{-1}, respectively. The optimum capacity for removal of glycerin could be achieved by using 4% (w/w) of D adsorbent and 20 minutes of contact time at 50°C. In addition, 98% of glycerin was removed by using 1% (w/w) of D adsorbent on the condition that methanol had been removed before treatment. Furthermore, by using 2% (w/w) of DDM 1.5 adsorbent and 10 minutes of contact time at 50°C, 28.92 % of monoglyceride could be removed. According to the adsorption isotherm, these processes are fit to both Fureundlich and Langmuir models.

This adsorption 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. The advantage over conventional water washing process is no wastewater generated from this adsorption process.

Field of Study : Environmental Management Student's Signature ....

Academic Year : 2009 Advisor's Signature ....

ACKNOWLDGMENTS

Firstly, I would like to express my deepest gratitude to my thesis advisor, Associate Professor Dr. Somchai Pengprecha, for his huge encouragement, invaluable supports, and kind guidance dedicated to me during my master degree learning. Not only did he teach me a lot of things regarding academic knowledge he has been an impressive example and role model for me which is better than wordy teaching and these made me develop my thoughts and my characters so much. He is not just only advisor but is one of the important persons that I respect beside my parents. This dissertation would have been accomplished without his excellent supervision.

I would like to thank Assistant Professor Dr. Narong Praphairaksit for teaching me about Atomic Absorption Spectroscopy (AAS). I also thank Dr. Manaskorn Rachakornkij, Dr. Chantra Tongcumpou, Dr. Nyein Nyein Aung, and Dr. Kunn Kangvansaichon for participating as my dissertation committee.

In addition, I desire to thank Program in Environmental Science and department of Chemistry, faculty of Science, Chulalongkorn University for the laboratory facilities. I also thank Graguate School, Chulalongkorn University for financial support.

Special thanks should also be directed towards my friends at the RCBC research group for their warm supports and imperative helps.

Finally, I feel proud to dedicate this thesis with all respects to my beloved parents for their love, encouragement, and inspiration throughout my entire study.

CONTENTS

Page

CHAPTER

CHAPTER Page

CHAPTER Page

CHAPTER Page

CHAPTER Page

LIST OF TABLES

Table Page

Table Page

LIST OF FIGURES

Figure Page

Figure Page

Figure Page

Figure Page

LIST OF SCHEMES

LIST OF ABBREVIATIONS

µl	microliter
µm	micrometer
AA	Atomic absorption spectometer
EN	The European Standard
°C	Degree Celsius
Co	initial sorbete concentration
Ce	Equilibrium concentration
DI	Deionized
FID	Flame Ionization Detector
FT-IR	Fourier Transform Infrared Spectroscopy
g	gram
GC	Gas-liquid chromatography
h	hour
kg/cm^3	Kilogram per cubic metre
k_f	Fruendlich consant
L	Liter
mole/L	mole per liter
min	Minute
mg	Miligram
ml	Milliter
mm	Millimeter
nm	Nanometer
ppm	parts per million
rpm	Revolution per minute
SEM	Scanning Electron Microscope
v/v	Volume by volume
w/v	Weight by volume
%wt	percent weight
AC	Activated Charcoal

D	Natural diatomite
DDM0.2	0.2 mole/L of $MnCl_2$ coating on diatomite adsorbent
DDM1.5	1.5 mole/L of $MnCl_2$ coating on diatomite adsorbent
DDM2.5	2.5 mole/L of $MnCl_2$ coating on diatomite adsorbent
Gb	Breakthrough value
Gc	Capacity value

CHARPTER I

INTRODUCTION

Previously, the price of the petroleum and the environmental concerns about pollution coming from the car gases continue to increase. Alternative fuel is the most possible way to solve these problems. Biodiesel, which is defined as a fuel consist of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats by using transesterification/ esterification reaction, is one of the possible way for this propose.

In the transesterification, triglycerides react with an alcohol, generally methanol or ethanol, to produce biodiesel and glycerol. The basic catalysts are the most generally used in synthesis biodiesel, because the process was proved to be faster. However, an excess amount of alcohol is usually used to drive the reaction towards the desired product.

After the completing of reaction, the biodiesel is brought to purify by water-washing to remove contaminants from biodiesel (See figure 1.1). However, the water-washing process has several disadvantages for example yields loss in effluent; high soap levels that cause emulsification and high cost of treatment. The water-washing process normally use large amount of water, and will generate wastewater that cause environmental problem.

To solve these problems, the research to date has tended to focus on using various adsorbents such as CaO, MgO, Mg_2CO_3, magnesium silicate, activated charcoal and bentonites to purify biodiesel instead of water washing process. In this study, natural diatomite, alternative low cost adsorbent available in Thailand, will be used. Furthermore, the effect of surface modification of diatomite by manganese on sulfur and metal ions adsorption will be studied.

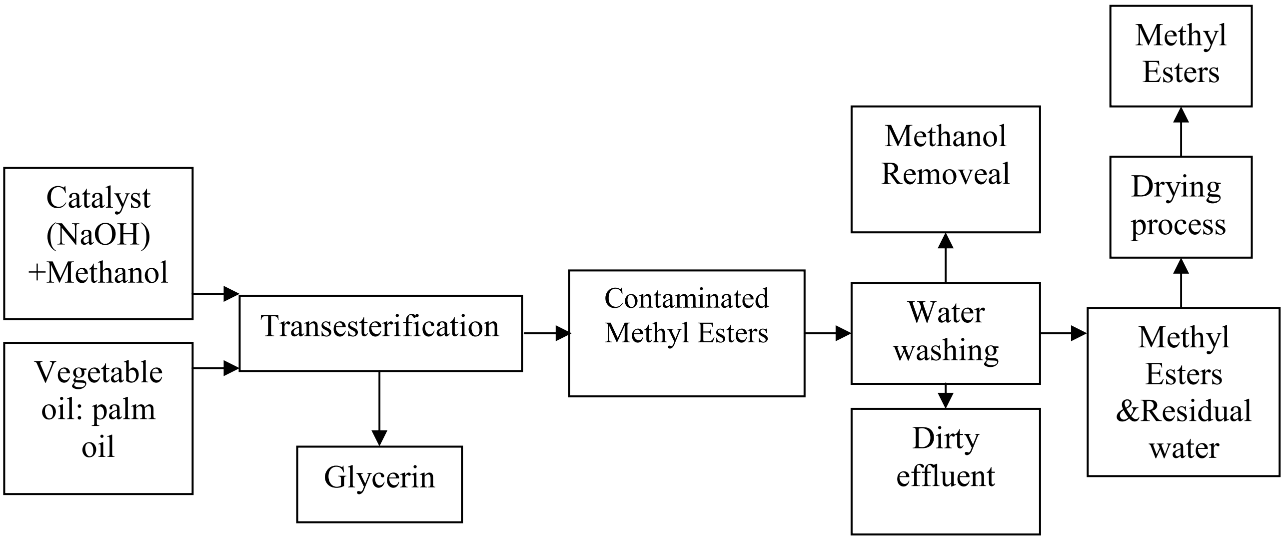


Figure 1.1 Biodiesel Production with water-washing process

Objectives

The overall objectives of this study are as follow:

1. To improve purification process by using adsorbent.
2. To study the preparation of MnO_2 doped diatomite adsorbent for biodiesel purification.
3. To determine the efficiency of natural diatomite adsorbent and MnO_2 doped diatomite adsorbent
4. To compare the performance of natural diatomite adsorbent and MnO_2 doped diatomite adsorbent with water-washing in biodiesel purification processes.

Scopes of this work

1. The preparation of MnO_2 doped diatomite adsorbent.
2. The synthesis of biodiesel by using base-catalyzed process.
3. The adsorption mechanism of glycerin and monoglyceride onto natural diatomite and modified diatomite were studied by mean of adsorbent isotherm.
4. The capability to adsorb glycerin between natural diatomite and activated charcoal will be compared.

Hypotheses:

Biodiesel can be purified by using natural diatomite adsorbent and MnO_2 doped diatomite adsorbent.

Benefits of this works

The results from this research clearly understand the adsorption behavior for glycerin and monoglyceride by using adsorbents. Moreover, this work also improves the adsorption capacity of low cost adsorbent by doping with manganese oxide which can be an effective adsorbent for monoglyceride removal in biodiesel. The outcome of this research can solve two environmental problems. Firstly, large amount of waste water was reduced since only was utilizes the adsorbent. Secondly, the cost of waste disposals was minimized.

CHARPTER II
THEORETICAL ASPECTS AND LITERATURE REVIEWS

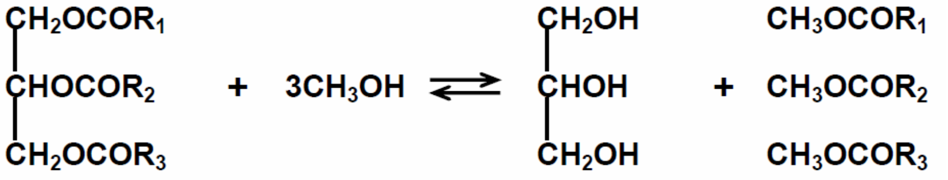
2.1 The production of biodiesel

The production of biodiesel typically uses transesterification process. Transesterification is the general term used to describe organic reactions where an ester is transformed into another ester through interchange of the alkoxy moiety as shown in Scheme 2.1 When the ester is reacted with an alcohol, this process is called alcoholysis.

$$\mathbf{RCOOR' + R''OH} \overset{\text{Catalyst}}{\longleftrightarrow} \mathbf{RCOOR'' + R'OH}$$

Scheme 2.1 General equations for transesterification reaction [1]

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of strong acid or base to give a mixture of fatty acids alkyl esters and glycerol as shown in Scheme.2.2 [1]. Alcohols can be used in the transesterification process which short chain such as methanol, ethanol, propanol and butanol. Methanol and ethanol were used most frequently, especially methanol because of its low cost and its physicals and chemical advantages [2]

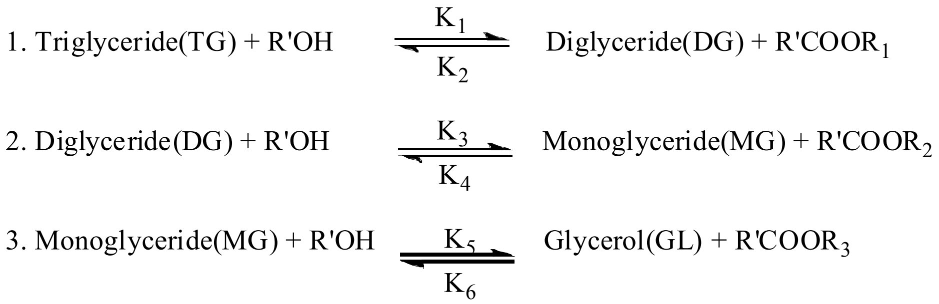


(Triglyceri)e) ***(methanol)*** ***(Glycerol)*** ***(biodisel)***

Scheme 2.2 Tranesterification reaction of triglyceride in the presence of sodium hydroxide (NaOH). [1, 3]

2.2 Transesterifcation kinetics and mechanism [4]

Fatty acid alkyl esters and glycerol is generated from transesterification of triglycerides . The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification was shown in Scheme 2.3 the first step is the conversion of triglycerides to diglycerides followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol yielding one methyl ester molecule from each monoglycerides at each step. The stepwise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order.



$$1.\ \text{Triglyceride(TG)} + \text{R'OH} \xrightleftharpoons[K_2]{K_1} \text{Diglyceride(DG)} + \text{R'COOR}_1$$

$$2.\ \text{Diglyceride(DG)} + \text{R'OH} \xrightleftharpoons[K_4]{K_3} \text{Monoglyceride(MG)} + \text{R'COOR}_2$$

$$3.\ \text{Monoglyceride(MG)} + \text{R'OH} \xrightleftharpoons[K_6]{K_5} \text{Glycerol(GL)} + \text{R'COOR}_3$$

Scheme 2.3 Transesterifcation kinetics and mechanism

2.3 Purification biodiesel process

The methyl esters cannot be classified as biodiesel until it meet specification of biodiesel standard. The untreated biodiesel contains several impurities: free glycerol, soap, metals, methanol, catalyst, water, and monoglycerides. Each impurity can cause engine as shown in Table 2.1 .Therefore, crude biodiesel need to purify before used. Two generally accepted methods to purify biodiesel are water- washing and dry – washing process [5]. Water-washing process is the process which a certain percentage of water is added to the crude biodiesel and the water is let to settle. This process is repeated until the water removed is clear in color. Dry-washing process is alternative process for purifying biodiesel by using various adsorbents such as CaO, MgO, Mg_2CO_3, magnesium silicate, activated charcoal and betonies [6, 7].

Table 2.1 Effect of impurities on biodiesel engines [8]

Impurity	Effect
Free fatty acids (FFA)	Corrosion, Low oxidation stability
Water	Hydrolysis (FFA formation) , Corrosion and Bacteriological growth (filter blockage)
Methanol	Low values of density and viscosity , Low flash point (transport, storage and use problems) , Corrosion of Al and Zn pieces
Monoglycerides	High viscosity, Deposits in the injectors (carbon residue) Crystallization
Metals (soap, catalyst)	Deposits in the injectors (carbon residue), Filter blockage (sulphated ashes), Engine weakening
Glycerol	Settling problems, Increase aldehydes and acrolein emissions

2.4 Adsorption phenomenon [9]

In general, adsorption is the process by which certain components of a fluid (liquid or gas) phase are transferred to and held at the surface of a solid. The adsorption process can be devided into three steps: 1) transfer of the adsorbate molecules through the film that surrounds the adsorbent; 2) diffusion through the pores if the adsorbent is porous; 3) uptake of the adsorbate molecules by the active surface, including formation of the bond between the adsorbate and the adsorbent. This general adsorption process is shown in Figure 2.1.

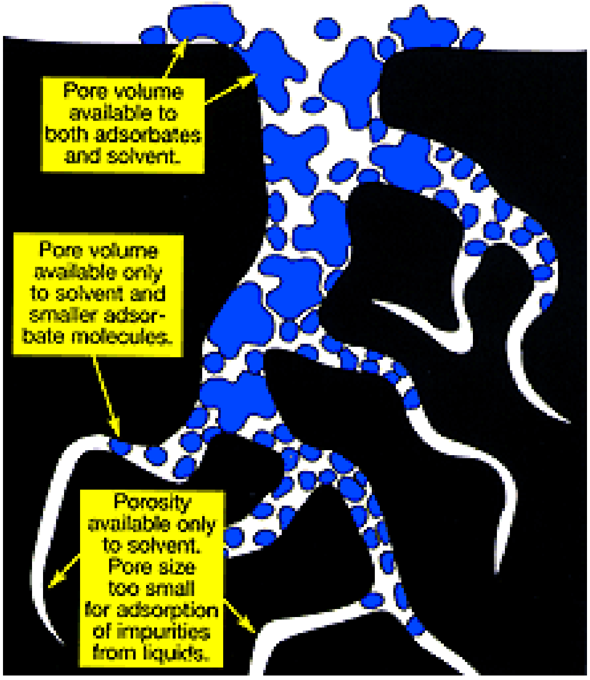


Figure 2.1 Adsorption process

In addition, the adsorption process can be classified into 2 types:

1. Physisorption (by van der Waals and electrostatic forces)

This is the most common form of adsorption. The molecules are attracted by van der Waals forces, and attach themselves to the surface of the solid. The molecules remain intact, and can be freed easily (the forces are small, and short-range).

2. Chemisorption (by chemical bonding)

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. If the molecules are removed, they may form different compounds.

2.5 Adsorption isotherm [10]

Equations that are often used to describe the experimental isotherm data were freundlich, Langmuir, and Brunauer,Emmet, and Teller (BET isotherm)

2.5.1 Freundlich Isotherm

Freundlich Isotherm is used most commonly to describe the adsorption characteristics of the activated carbon used in water and wastewater treatment. Derived empirically in 1912, the Freundlich isotherm is defined as follow:

$$x/m = K_f C_e^{1/n} \qquad (2.1)$$

where x/m = mass of adsorbate adsorbed per unit mass of adsorbent, mg $_{\text{adsorbate}}$/ mg $_{\text{adsornent}}$

K_f , n = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

The constant in the Freundlich isotherm can be determined by plotting (x/m) versus C_e (as show in Figure 2.2) and making use of Equation. (2.2) rewritten as the following equation(Metcalf & Eddy, 1991)

$$\log(x/m) = \log K_f + (1/n)\log C_e \qquad (2.2)$$

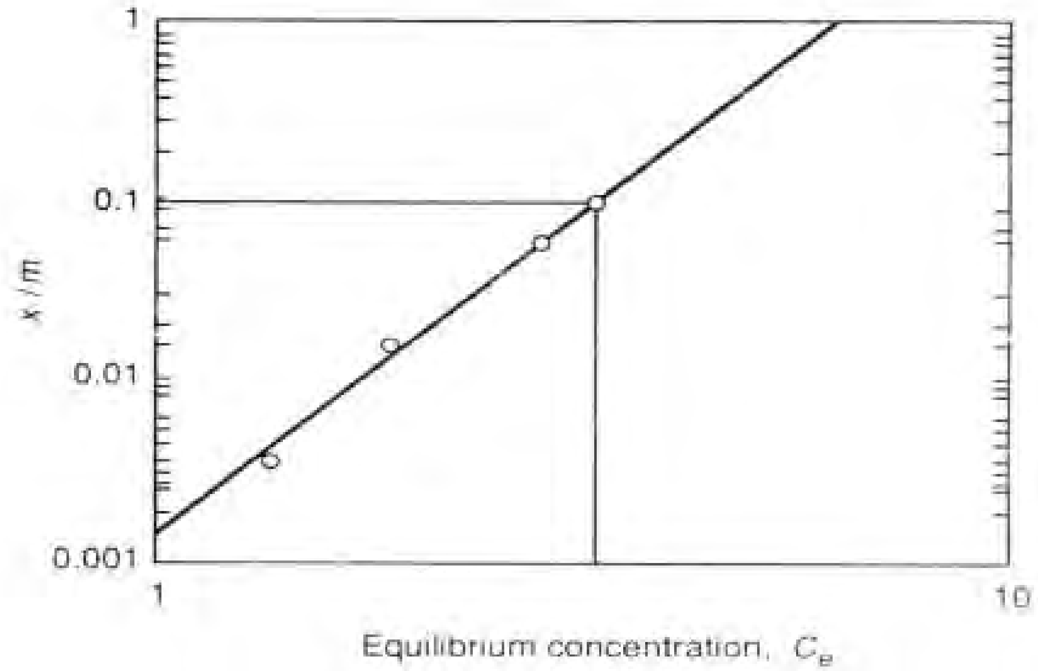


Figure 2.2 Freundlich isotherms [11]

2.5.2 Langmuir isotherm

Langmuir isotherm derived from rational considerations , the Langmuir isotherm is defined as :

$$x/m = (abC_e)/(1+bC_e) \qquad (2.3)$$

where

x/m = mass of adsorbate adsorbed per unit mass of adsorbent, $\text{mg}_{\text{adsorbate}}/\text{mg}_{\text{adsornent}}$

a, b = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

The Langmuir adsorption isotherm was developed by assuming: A fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy.

Adsorption is reversible

Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface. The rate at which adsorption proceeds is proportional to the driving force, which is the difference between the amounts adsorbed at a particular concentration, and the difference is zero. The constants in the Lengmuir isotherm can be determined by plotting Ce/(x/m) versus Ce (as show in Figure 2.3) and making use of Equation. (2.4) (Metcalf & Eddy, 1991)

$$Ce/(x/m) = 1/(ab) + (1/a)C_e \qquad (2.4)$$

The important characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L [17]

$$R_L = 1/(1+bCo) \qquad (2.5)$$

where

Co is the highest initial concentration (g/L).

Table 2.2 Term of a dimensionless factor of Langmuir isotherm

RL	Type of isotherm
RL>1	Unfavorable
RL=1	Linear
0<RL<1	Favorable
RL=0	Irriversible

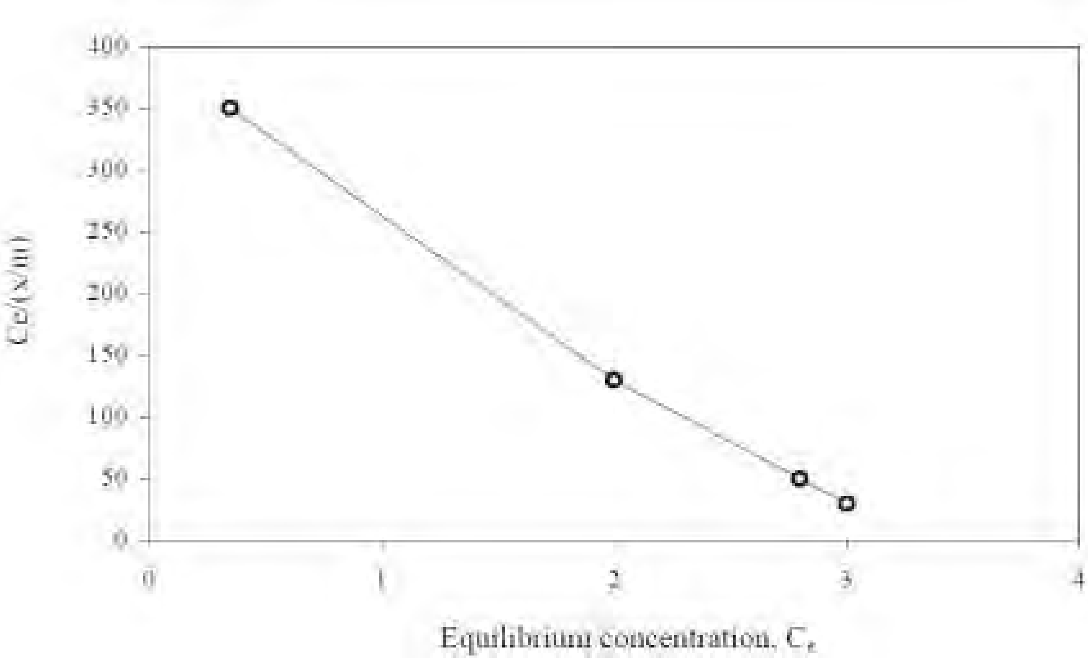


Figure 2.3 Langmuir isotherm [11]

2.6 Adsorption/desorption isotherm [11, 12]

The adsorption/desorption isotherm shows the relationship between the amount of adsorbed/desorbed gas (y-axis) and the pressure of adsorptive (x-axis) at the constant temperature.

2.6.1 BET Theory

The BET analysis is the standard method for determining surface areas from nitrogen adsorption isotherms and was originally derived for multilayer gas adsorption onto flat surfaces. (Walton KS, Snurr RQ). The BET equation has been utilized in determining the monolayer volume of adsorbed gas, consequently we can calculate the surface area of adsorbent.

The BET equation was derived on the following hypothesis:

1. Surface is energetically homogeneous.
2. There is no lateral interaction between adsorbed molecules.
3. The adsorption energies in the second and all higher layers are equal to condensation energy of adsorptive.

2.7 Adsorption, Surface Area, and Porosity

In physical adsorption, adsorption isotherm can be classified as one of 6 types, as show in Figure 2.4. Table2.3 shows the types and features, as well an adsorbent example.

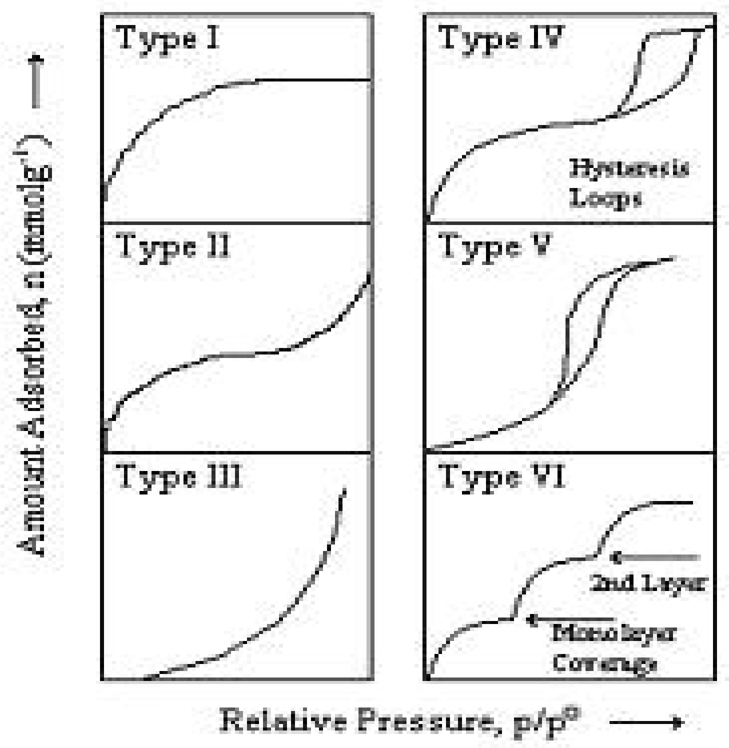


Figure2.4 IUPAC classification of adsorption isotherms

Table 2.3 Feature of adsorption isotherms [13]

Type	**Features**		**Sample-Adsorptive example**
	Interaction between samples surface and Adsorbate	**Porosity**	
I	Relative strong	Micropores	Activated carbon-Nitrogen
II	Relative strong	Nonporous	Oxide-Nitrogen
III	Weak	Nonporous	Carbon-Water vapor

Table 2.3 Feature of adsorption isotherms (continues)

Type	Features		Sample-Adsorptive example
	Interaction between samples surface and Adsorbate	**Porosity**	
IV	Relative strong	Mesopore	Silica-Nitrogen
		Mesopore	
V	Weak	Micropore	Activated carbon-Water vapor
VI	Relative strong Sample surface has an even distribution of enregy	Nonporous	Graphite-Krypton

Adsorption isotherms are classified as shown in Table 2.4 based on the strength of the interaction between the sample surface and adsorptive, and the existence or absence of pores. However, some actual samples do not fit into adsorption isotherm type I to IV. These may be measured as mixed types of adsorption isotherm. For example, nitrogen adsorption for a porous sample with large external surface area may generate a compound isotherm resembling types I and II, or type I and IV. To analyze an adsorption isotherm, it has to assume certain sample features, such as the pores from the shape of the isotherm. Then, analyze the adsorption isotherm using an appropriate analysis method.

Table 2.4 IUPAC classification of pores

Types	Pore diameter/nm
Micropore	Up to 2
Mesopore	2 to 50
Maccropore	50 or up

By measuring nitrogen adsorption isotherms, a type I, II, IV adsorption isotherm can be measured mainly and sample information containing a specific surface area and porous structure will be obtained. Table2.3-2.5 Briefly sums up what analysis data can be obtained from a nitrogen adsorption isotherm.

Table2.5 Analysis Data obtained from a nitrogen adsorption isotherm

Type of adsorption isother	**Sample information**	**Analysis method**	**Major analyzed data**
Type I	Total specific surface area	BET plot	a_{s}, BET [m^2g^{-1}]
	Total specific surface area	t plot, a_s plot	a_1 [m^2g^{-1}]
	External specific surface are	t plot, a_s plot	a_2 [m^2g^{-1}]
	Micropore area	t plot, a_s plot	$a_1 – a_2$ [m^2g^{-1}]
	Micropore volume	t plot, a_s plot	v_2 [cm^3g^{-1}]
	Micropore width	t plot	2t[nm]
	Micropore distribution curv	MP plot	Micropore range
	Micropore distribution peak	MP plot	$d_{p\ peak}$ or r p$_{peak}$[nm]
	Micropore volume	DA plot	v_p [cm^3g^{-1}]
	Micropore distribution curv	HK plot	Micropore range
	Micropore distribution peak	HK plot	$d_{p\ peak}$ or r p$_{peak}$[nm]
	Micropore distribution curv	SF plot	Micropore range
	Micropore distribution peak	SF plot	$d_{p\ peak}$ or r p$_{peak}$[nm]
Type II	Total specific surface area	BET plot	a_{s}, BET [m^2g^{-1}]
	Total specific surface area	t plot, a_s plot	a_1 [m^2g^{-1}]

Table2.5 Analysis Data obtained from a nitrogen adsorption isotherm (continuous)

Type of adsorption isother	**Sample information**	**Analysis method**	**Major analyzed data**
Type IV	Total specific surface area	BET plot	a_s, BET [m^2g^{-1}]
	Total specific surface area	t plot, a_s plot	a_l [m^2g^{-1}]
	Mesopore distribution curve	BJH plot, DH plot, Cl plot	Mesopore range
	Mesopore distribution peak	BJH plot, DH plot, Cl plot	$d_{p\,peak}$ or $r\,p_{peak}$[nm]
	Mesorore volume	BJH plot, DH plot, Cl plot	v_p [cm^3g^{-1}]
	Mesopore area	BJH plot, DH plot, Cl plot	a_p [m^2g^{-1}]

2.8 Breakthrough and Adsorption capacity [11]

Typically, breakthrough occurred when the effluent concentration reaches 5 percent of the influent value. Exhaustion or adsorption capacity of the adsorption bed is assumed to have occurred when the effluent concentration is equal to 95 percent of the influent concentration. (14). Typical breakthrough curve and capacity were shown in Figure 2.5.

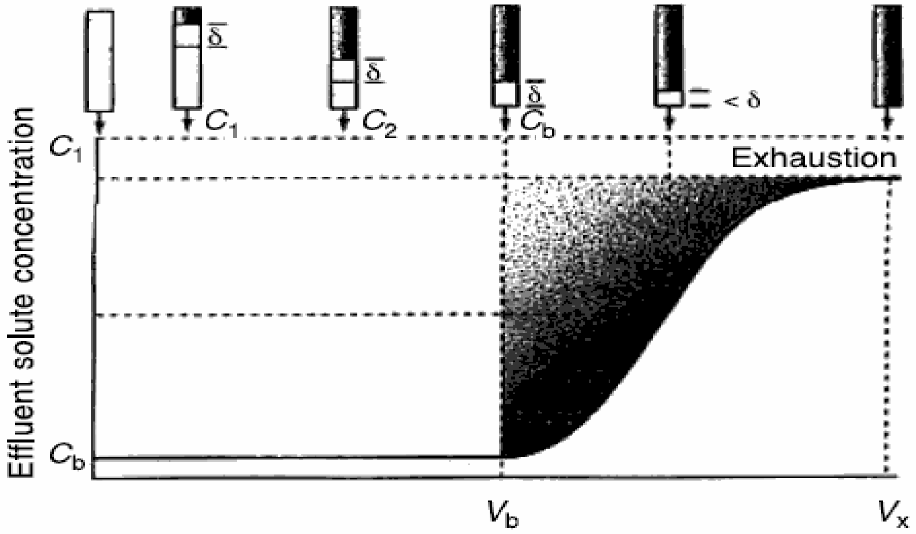


Figure 2.5 Typical breakthrough curve and capacity

2.9 Activated charcoal [11]

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 hole molecules, which remain in place by van der Waals forces (physisorption). Activated charcoal is prepared by first making a char from organic materials such as almond, coconut, and walnut hulls; other materials including wood, bone, and coal have also been used. The activated charcoal is produced by heating material to a red heat (less than about 700 ^{o}C) in a retort to drive off the hydrocarbon but without oxygen under N_2 atmosphere. The carbonization or char-producing process is essentially a pyrolysis process. the char particle is then activated by exposure to oxidizing gases such as stream and CO_2 at high temperature , in the rang of 800 – 900 ^{o}C . These gases develop a porous structure.

2.10 Natural diatomite [7]

Natural diatomite ($SiO_2.nH_2O$), or diatomaceous earth, is a soft lightweight rock available in large deposits around the world and the chemical composition of natural diatomite was showed in Table 2.6 This pale colored sedimentary rock consists principally of silica microfossils of aquatic, unicellular alga varying in shape and size of diatomite. Diatomite is highly porous (see Figure 2.6-2.7), with its structure containing up to 80–90% voids. It is used in a number of industrial applications, e.g. as a filtration media for various beverages, and inorganic and organic chemicals, and as an adsorbent for pet litter and oil spills. Although diatomite has a unique combination of physical and chemical properties, its use as an adsorbent in wastewater treatment has not been extensively investigated.

Figure 2.6 Natural diatomite

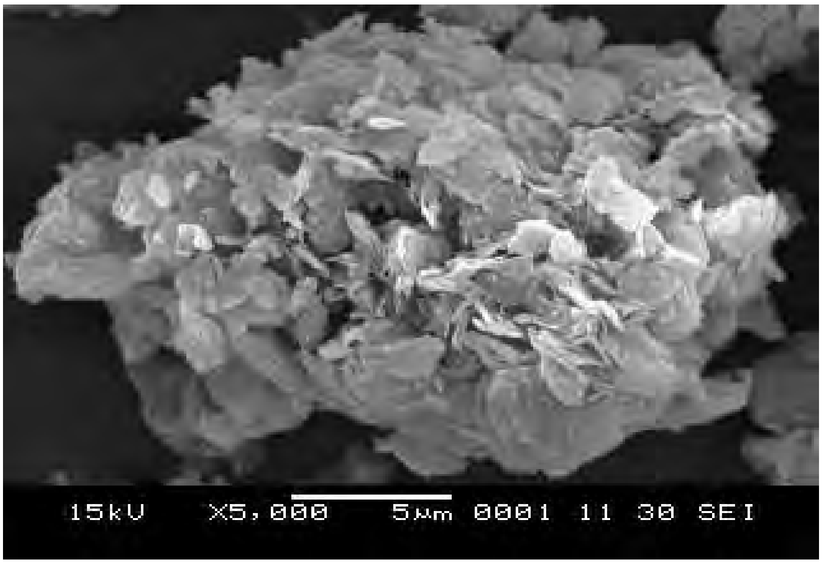


Figure 2.7 Scanning electron micrograph of diatomite (magnification 5000x).

2.10.1 The filter aid property of diatomite

The filter aid property of diatomite was listed below:

1. Filter aid is used to remove the suspending impurities in microns from any liquid.

2. In pharmaceuticals, it is used to filter syrups and other bulk drugs in liquid form, which is added in Tablets etc.
3. In oil Industries, before packing, it is used to filter oil to give it a shine and to remove any suspending impurity.
4. Beer is filtered through diatomite before packing to remove molasses.
5. Filter candles are made from diatomite filteraids for drinking water purification.
6. Processed diatomite granules 15 to 50 mm are used in denim cloth wash, to give it shine and design. Diatomite granules are replacement of pumice stone which is used for same purpose and is imported from turkey.

Table 2.6 Chemical composition of natural diatomite [5].

Oxide	**Composition (%)**
SiO_2	72.50
Al_2O_3	11.42
Fe_2O_3	5.81
MgO	0.25
CaO	1.48
Na_2O	7.21
K_2O	0.69

2.11 Biodiesel quality

Due to the fact that biodiesel is produced in quite differently scaled plants from vegetable oils, it was necessary to install a standardization of fuel quality to guarantee engine performance. Generally, it use ASTM D6751 but several countries in Europe did establish standards for biodiesel such as Austria, Sweden. For Thailand, it has set legislative assembly characteristic and quality of biodiesel as shown in Table 5.

Table 2.7 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand [13].

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 D 445
Flash Point, ^{o}C	> 120	ASTM D 93
Sulphur, %wt.	< 0.0010	ASTM D 2622
Carbon Residue, on 10% distillation residue, %wt	< 0.30	ASTM D 4530
Cetane Number	> 51	ASTM D 613
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

Methyl ester: The purpose of this EN is to determine the ester content of fatty acid methyl ester intended for use as pure biofuel or as a blending component for heating and diesel fuels. Determination of the percentage of methyl ester of fatty acid present in the sample by gas chromatography with internal calibration.

Total glycerin – “is the sum of free and bonded glycerin.” Bonded glycerin – “is the glycerin portion of the mono-, di-, and triglyceride molecules.” Elevated total glycerin values are indicators of incomplete esterification reactions and predictors of excessive carbon deposits in the engine. The terms “glycerin” and “glycerol” are used interchangeably.

Water and sediment is a test that “determines the volume of free water and sediment in middle distillate 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.” This test is a measure of cleanliness of the fuel. For B100 it is particularly important because water can react with the esters, making free fatty acids, and can support microbial growth in storage tanks.

Phosphorus – “This test covers the quantitative determination of barium, calcium, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additive packages.” In the case of B 100, phosphorus can come from incomplete refining of the vegetable oil and from bone and proteins encountered in the rendering process.

2.12 Literature Reviews

In 2001, AL-DEGS *et al.* [11] studied sorption of lead ions on diatomite and manganese oxide modified diatomite. Diatomite and manganese oxides modified diatomite are effective adsorbents for removing lead ions from solution. The sorption capacity of diatomite and modified diatomite were 24 and 99mg g_1 for lead ions, respectively. The high increase in sorption efficiency of Mn-diatomite was attributed to high negative surface charge on the modified surface.The filtration quality of diatomite has significantly improved after modification.

In 2003, Maskan and Bagci [7] studied the refining of used sunflower seed oil by various adsorbents (CaO, MgO, Mg_2CO_3, magnesium silicate, activated charcoal and permez earth). Permez earth, magnesium silicate and bentonite exhibited the highest abilities in decreasing oil viscosity, FFAs reduction and colour recovery, respectively.

In 2005, Bertram *et al.* [10] disclosed methods of purifying biodiesel fuel by using at least one adsorbent, such as magnesium silicate, silica gel, metal hydroxides and other materials. As water washing process has several limitations, including high soap levels that cause emulsification; high effluent treatment and disposal cost; decreased yields. To avoid the limitations of water-washing process, 1% MAGNESOL treated methyl ester was met all ASTM specifications

In 2005 Ahmad *et al.* [11] synthesized rubber powder which was used to adsorb the oil residual in palm oil mill effluent. The adsorption process was studied by varying parameters, such as adsorbent dosage, mixing speed, mixing time and pH. It was found that removal of residual oil was obtained with an adsorbent dosage of 30 mg dm-3 and mixing speed of 150 rpm for 3 h at pH 7.

In 2006, Moslehi and Nahid [5] studies the efficiency of Iranian diatomite soil and the form modified by Mn oxide as an adsorbent and a filtration agent for the purpose of Pb, Ni and Cu removals from water and wastewater. It found that when diatomite is modified by manganese oxide its absorption capacity goes up, and this was due to an increase in surface area and also increasing the surface change. Filtration quality of diatomite is also increased after modification with Mn oxide.

In 2007, Marchetti et al. [3] made a review of the possible methods that could be used to produce biodiesel. Different studies have been carried out using different oils as raw material, different alcohols (methanol, ethanol, and buthanol) as well as different catalysts, homogeneous, and heterogeneous processes were used. The advantage and disadvantage of each method was reported. The concluded that alkyl catalyzed reaction is a vary good process of production with relatively high conversion.

In 2008, Berriosa and Skeltonb [8] studied the comparison of purification methods for biodiesel. Three methods of purification using; water wash, ion-exchange resins, and magnesium silicate have been investigated under several reaction conditions (temperature, concentration, agitation rate, etc.) It has been shown that three methods can remove glycerol and soap contents down to the requirement of EN 14214 standard.

In 2009, Yehya et al. [29] studied mechanism and chemistry of manganese oxides-modified diatomite (MOMD) to remove basic and reactive dyes from aqueous solution. The adsorption capacity of MOMD for methylene blue (MB), hydrolysed reactive black (RB) and hydrolysed reactive yellow (RY) was 320, 419, and 204 mg/g, respectively. Basically, two mechanisms may be occurring: 1) intercalation of dye in the octahedral layers and 2) adsorption of dye on the MOMD external surface. Furthermore, FTIR and pH analyses suggested that the adsorption of MB, RY, and RB onto MOMD may be occurred by the formation of a monodentate, bidentate, and tridentate, respectively. The determination of sodium ions in the equilibrium dye solution might be an extremely sensitive fingerprint for the detection of the adsorption mechanism of dye adsorption onto MOMD.

In 2009, Xiangying Zenga and Yuehua Fan [30] studies the effectiveness of local diatomite modified by microemulsion and manganese oxide for the removal of chromium ion (III) from aqueous solution. It found that the surface areas of diatomite were increased due to the formation of the manganese oxides on the diatomite surface in MnD and corresponding to the present hydrolyzed aromatic acid in DMM respectively. Within the experimental range of pH (pH = 2.2–6.3), the chromium ion (III) removal of DMM (varying from 35% to 70%) was higher than that of MnD (varying from 33% to 59%) due to the different electrostatic forces between chromium ion (III) and the surfaces of the modified diatomite.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials and equipments

3.1.1 Raw material

- Palm cooking oil
- Natural diatomite, Lumpang province Thailand

3.1.2 Chemical Reagents

- Anhydrous sodium sulfate: analytical grade; Carlo Erba
- Sodium hydroxide: analytical grade; ACS
- Ethanol: analytical grade; Merck
- Heptane: analytical grade; Merck
- Hexane: analytical grade; Lab-Scan
- Hydrochloric acid: analytical grade; Merck
- Acetic acid: analytical grade; Merck
- Methanol: analytical grade; Merck
- Deionized water (DI water)
- Isopropyl alcohol (IPA); commercial grade
- Phenol Read Indicator; May & Baker
- Bromophenol blue: analytical grade; CarolBrba
- Mn (IV) Cl: analytical grade; Carol Erba
- Manganese nitrite: analytical grade; BDTL chemical LTD Poole/ England

3.1.3 Equipments

- Gas-liquid Chromatography; Model 3800; Varian
- Rotary evaporator: Model ; Buchi
- Magnetic stirrer
- Water bath and shaker ; Mammert W350, Germany
- Atomic absorption spectrometer (AA); Perkin Elmor

- X-Ray Diffractometer (XRD);Perkin Elmor
- Scanning Electron Microscope (SEM) /JEOL/JSM-6480LV
- BET (using BELSORP analysis program)
- Fourier Transform Infrared Spectroscope (FT-IR); Nicolet

3.1.4 Glassware

- Volumetric flasks
- Filtering Flasks
- Glass watches
- Beakers
- Pipettes
- Dropper
- Separation funnel
- Reflux condenser
- Round bottom flask
- Funnel
- Burette
- Syringe
- Micro pipettes
- Thermometer
- Sieve (100 meshes)

3.2 Methods

3.2.1 Preparation of natural diatomite adsorbent

The natural diatomite adsorbent was washed with DI water, dried at 100^0C for 4h. The obtained diatomite was then ground, screened through 100 mesh sieve and stored in tightly capped glass bottle for future use.

3.2.2 Preparation of MnO_2 doped diatomite adsorbent

15 g of natural diatomite was immersed in sufficient 6M sodium hydroxide at 80^oC for 2 h. The mixture was placed in 100 mL of 2.5 M manganese chloride (pH adjusted to 1–2 with hydrochloric acid) at room temperature for 10 h.

The manganese-soaked diatomite was collected by filtration. It was then immersed in 6 M sodium hydroxide at room temperature for 10 h to precipitate manganese hydroxide. The supernatant was decanted and diatomite was left exposed to air to facilitate oxidation of manganese hydroxide to a mixture of hydrated manganese oxides for 48 h. Then the sample was washed with excess of DI water until pH 7. Then the sample was dried at 100 °C, and desiccated. The obtained MnO2 doped diatomite adsorbent was then ground, screen through 100 mesh seive and stored in tightly capped glass bottle for future use. For the different loading manganese oxide, 0.2 and 1.5 M $MnCl_2$ were used instead of 2.5 M $MnCl_2$.

3.2.3 Determination of the amount of manganese oxides on diatomite

3.2.3.1. 10, 8, 6, 4, and 2 ppm of working standard solution

- 100 ppm of manganese nitrite stock standard solution :

10 ml of 1000 ppm of manganese nitrite standard solution was pipetted into a 100 ml of volumetric flask and make up volume with DI water.

- 10 ppm of manganese nitrite standard solution:

10 ppm of 100 ppm of manganese nitrite stock standard solution was pipetted into a 100 ml of volumetric flask and make up volume with DI water.

- 8 ppm of manganese nitrite standard solution:

8 ppm of 100 ppm of manganese nitrite stock standard solution was pipetted into a 100 ml of volumetric flask and make up volume with DI water.

- 6 ppm of manganese nitrite standard solution:

6 ppm of 100 ppm of manganese nitrite stock standard solution was pipetted into a 100 ml of volumetric flask and make up volume with DI water.

- 4 ppm of manganese nitrite standard solution:

4 ppm of 100 ppm of manganese nitrite stock standard solution was pipetted into a 100 ml of volumetric flask and make up volume with DI water.

- 2 ppm of manganese nitrite standard solution:

2 ppm of 100 ppm of manganese nitrite stock standard solution was pipetted into a 100 ml of volumetric flask and make up volume with DI water.

All of working standard solutions were measured by AAS, and the standard curve was constructed by plotting the intensities versus concentration of working standard solutions.

3.2.3.2 Sample preparation of manganese ion

The amount of manganese oxides doped on the natural diatomite was determined by dissolving 0.1 g of each modified diatomite (DDM0.2, DDM1.5, and DDM 2.5) in 100 ml of 4 M hydrochloride acid digested at 40^{o}C for 0.5 h. and filtered, 10 ml of filtered was pipetted in to 1000 ml of volumetric flask and make volume up with DI water. The solution mixture was serially diluted until the designed concentration was obtained

3.2.4 Characterization of natural diatomite and modified diatomite

The effect of chemical modification on natural diatomite was characterized by, scanning electron microscopy (SEM), fourier-Transform Infrared spectrometer (FT-IR spectrometer), BET method, and X-Ray Diffractometer (XRD).

3.2.4.1 By scanning electron microscopy (SEM)

The samples were coated with gold (Au) and analyzed by SEM.

3.2.4.2 By fourier-Transform Infrared spectrometer (FT-IR spectrometer).

FT-IR spectra of natural diatomite and modified diatomite were recorded from 4000-400cm^{-1} on KBr pellet.

3.2.4.3 By X-Ray Diffractometer (XRD)

XRD analysis was carried out using Diffractometer 5000D, Cu K&1 radiation (a = 40kV, 30mA) and the sample was scanned from 5^{0} to 50 ^{0} (2 theta) in step size of 0.020 ^{0}.

3.2.4.4 By BET method

The Characterization of natural diatomite and modified diatomite according to BET method can be carried out into two steps: pretreatment and surface area analyzer.

Step1, Pretreatment; 40 milligrams of each adsorbent was accurately weighed (0.04xxg) into sample cell, then the sample cells were connected with connection tube to evacuate the air and then heat at 400^{o}C for 3 hr.

Step2, Surface area analyzer; sample cell was accurately weighed after complete pretreatment. Next, sample cell was connected on BELSORP instrument for calculated surface area.

3.3 Synthesis of biodiesel from palm oil via base-catalyzed process

Palm oil (400 g) was added into 1000 mL of round bottom flask equipped with condenser. After the oil was heated to 65 °C, the solution of sodium hydroxide (4.0g) in methanol (115.85 mL) was slowly added into the reaction and then the mixture was heated to 65°C for 1.5 h. The reaction mixture was transferred to a separatory funnel. After 0.5 h the glycerin layer was then separated to yield crude biodiesel (93-94%wt).

3.4 Purification processes

3.4.1 Water-washing process

In a 500 mL separation funnel, 100 g of dionised water was washed with DI water (15x 100) at room temperature. The biodiesel was dried on Na_2SO_4 and filter to yield pure biodiesel (93-94%wt).

3.4.2 Dry-washing experiment (Glycerin & monoglyceride adsorption)

Dry-washing experiment was classified in to 2 process; glycerin adsorption using natural diatomite and glyceride adsorption using natural diatomite doped with manganese oxide.

3.4.3 Glycerin purification process

The adsorption of glycerin was by using natural diatomite adsorbent with optimizing various parameters: temperature, contact time, adsorbent dose. In addition, the adsorption process was compared with water washing process.

3.4.3.1 Effect of Temperature on precipitation of glycerin at various temperatures in close and open systems

100 g of crude biodiesel in close and open systems was immerged in water bath and the temperature was set at room temp., 40, 50, and 60^{o}C. Every 10 minutes, about 3 g of each of sample was sampling to determine glycerin content by using titration method (3.5.1)

3.4.3.2 Effect of contact time on glycerin adsorption

50 g of crude biodiesel was treated with 2% (w/w) of natural diatomite, DDM 2.5 and various contact times: 10, 20, and 30 minutes. Then the adsorbent was removed by filtration. The glycerin content was determined by titration method (3.5.1).

3.4.3.3 Effect of concentration of natural diatomite and DDM 2.5 adsorbent for glycerin adsorption (direct treatment)

In an effort to adsorb glycerin, five concentrations of each adsorbent: 1, 2, 3, 4 and 5 %wt were used. In a 150 mL flask, 50 g of crude biodiesel was treated with each adsorbent at 50^{o}C, with stirring at 150 rpm and contact time at 20 minutes in water bath. Then the adsorbent was removed by filtration. Samples were analyzed using titration method and GC method (3.5.1).

3.4.3.4 Treatment after methanol removal

The excess methanol in crude biodiesel was removed by rotary evaporator at 50^{o}C, and then the crude biodiesel was brought to purification process. In a 100 mL glass bottle, 50 g of crude biodiesel was treated with natural diatomite adsorbent (0.2, 0.4, 0.6, 0.8 and 1 %wt) at 50^{o}C, with stirring rate at 150 rpm and contact time at 20 minutes in water bath. Then the adsorbent was removed by filtration. Samples were analyzed using titration (3.5.1) and GC method (3.5.2).

3.4.3.5 Breakthrough point and capacity of natural diatomite for glycerine adsorption

In 100 ml glass bottom, 30g of crude biodiesel was treated with 1g of natural diatomite at 50 ^{o} C for 10 minutes. After that, crude biodiesel was poured out. Then, 30 g of crude biodiesel was treated with used natural diatomite at the same condition. This process was repeated until the effluent concentration reaches 5 percent of the influent value. Exhaustion or capacity of the adsorbent was occurred when the effluent concentration reaches 95 percent of the influent concentration. Samples were analyzed using titration method (3.5.1)

3.4.3.6 Adsorption isotherm glycerin

In a 100 mL glass bottom, 30 g (4500 ppm) of crude biodiesel was added in to varied concentration of natural diatomite (1, 2, 3, 4, 5, 6, 7, 8, 9and 10 %wt), at 50 ^{o}C, with stirring at 150 rpm and contact time at 20minutes. The adsorbent was removed by filtration and the amount of residuals glycerin were analyzed by using titration method (3.5.1)

3.4.4 Monoglyceride purification process

Before study the adsorption of monoglyceride,the glycerin and free glycerol in crude biodiesel were removed by using dry-washing and water-washing processes. This biodisel refer to treated biodiesel.

3.4.4.1 Comparisons of various types of adsorbent on adsorption of monoglyceride

10 g of treated biodiesel was treated with 5% (w/w) of different type of adsorbents: natural diatomite, burnt natural diatomite, and modified diatomite at 50^{o}C with stirring rate at 150 rpm and contact time at 10 minutes in water bath. Then the adsorbent was removed by filtration. Samples were analyzed by GC method (3.5.2).

3.4.4.2 Effect of contact time for the adsorption of monoglyceride with MnO_2 doped diatomite

10 g of treated biodiesel was treated with 5 %(w/w)of natural diatomite doped with manganese oxide (DDM 1.5) at various contact times: 5, 10, 15 and 20 minute at 50^{o}C, with stirring rate at 150 rpm in water

bath. Then the adsorbent was removed by filtration. Samples were analyzed by using GC method (3.5.2)

3.4.4.3 Effect of $MnCl_2$ concentration doped on natural diatomite for monoglyceride removal

10 g of treated biodiesel was treated with 5 percent of different doped manganese oxide on diatomite: 0.2M, 1.5M, and 2.5M, at 50°C with stirring at 150 rpm for 10 minutes in water bath. Then the adsorbent was removed by filtration. Samples were analyzed by GC method (3.5.2).

3.4.4.4 Effect of concentration of DDM 1.5 for monoglyceride removal

10 g of treated biodiesel treated with various concentration of DDM 1.5 (2, 4, 5, 6, 7, 8, 9, and 10 % wt.) at 50°C with stirring at 150 rpm for 10 minutes in water bath. Then the adsorbent was removed by filtration. Samples were analyzed by GC method (3.5.2).

3.4.4.5 Adsorption isotherm of monoglyceride

The adsorption isotherms were studied to evaluate the adsorption capacity of natural diatomite and modified diatomite for glycerin and monoglyceride removal from biodiesel production.

In a 50 mL glass bottom, 10 g (0.83%mono) of crude biodiesel was added in to varied concentration of modified diatomite (, 2, 5, 6, 7, 8, 9and 10 %wt), at 50 °C, with stirring at 150 rpm and contact time at 10minutes. The adsorbent was removed by filtration and the amount of residuals monoglyceride were analyzed by using GC method (3.5.2)

3.5 Analytical methods

3.5.1 Titration method

(A two-step) Titration method is used to determine the amount of glycerin and unreacted catalyst. In Step 1, 3 g of crude biodiesel 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 colorless. Then in Step 2, 1 mL of 0.04%bromophenol blue was added into the mixture. The solution was further 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” [5]. The mount of unreacted NaOH can be calculated by using equation 1:

$$\text{g of NaOH / g of crude biodiesel} = \frac{\text{A x 0.01 x 40.0}}{\text{W x 1000}} \qquad (1)$$

where:
A = volume of hydrochloric acid used in step 1.
W = weight of crude biodiesel used (g).

And the amount of glycerin in the biodiesel can be calculated by using equation 2:

$$\text{g of glycerin /g of crude biodiesel} = \frac{\text{B x 0.01 x304.4}}{\text{W x 1000}} \qquad (2)$$

where:
B = volume of hydrochloric acid used in step 2.
W = weight of crude biodiesel used (g).

3.5.2 Gas chromatograph method

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).

100 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/minutes The detector temperature was set to 380 °C and the total run time was 36 minutes.

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:

GT = 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

CHAPTER IV

RESULTS AND DISSCUSSION

4.1 Characterisation of natural diatomite and modified diatomite

4.1.1 By Scanning electron microscope

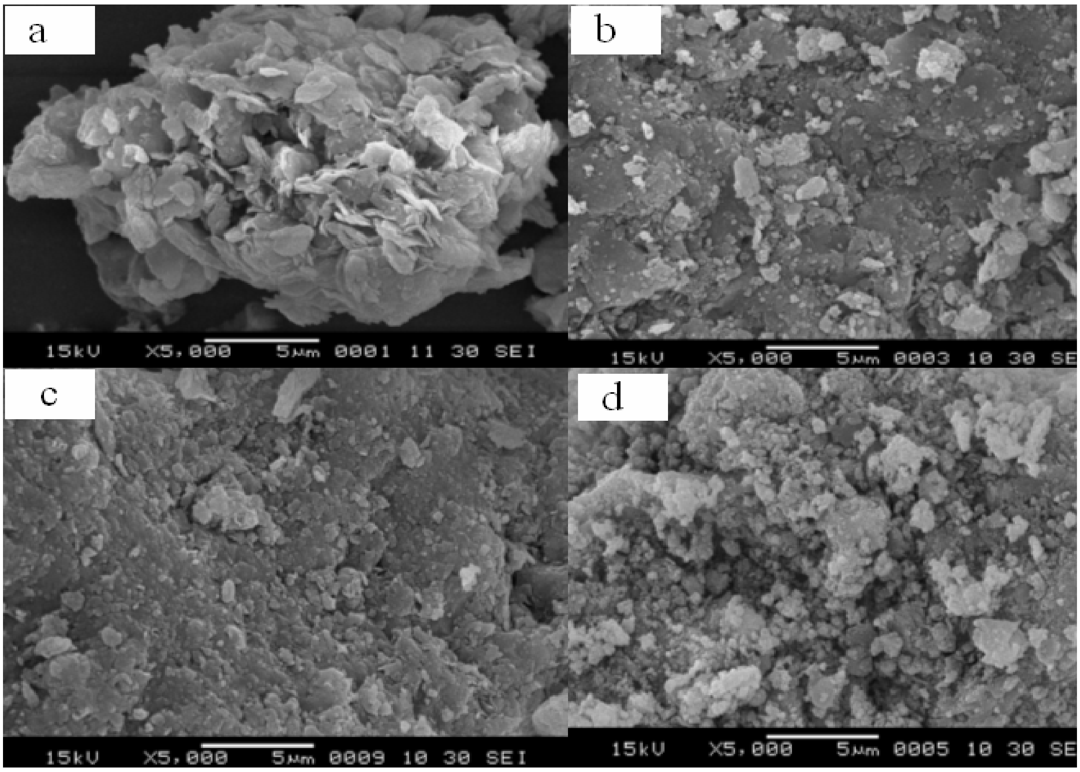


Figure 4.1. Scanning electron micrograph of natural diatomite (a); DDM 0.2 (b); DDM 1.5 (c); DDM 2.5 (d) (magnification 5000X)

The scanning electron macrograph of natural diatomite DDM 0.2, DDM 1.5 and DDM 2.5 are shown in Figure 4.1, Natural diatomite consists of wide variety of petal shapes and sizes with smooth surface (1-3 µm). However DDM 0.2, DDM 1.5 and DDM 2.5 have a surface roughness and small particle, typically 0.1-1µm

4.1.2 By X – Ray diffraction (XRD)

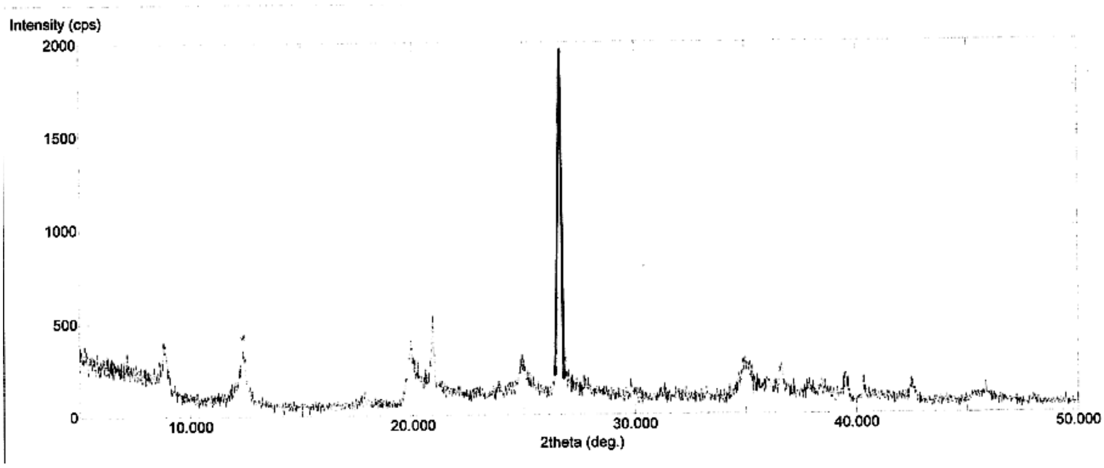


Figure 4.2 XRD pattern of natural diatomite (*SiO_2 peaks)

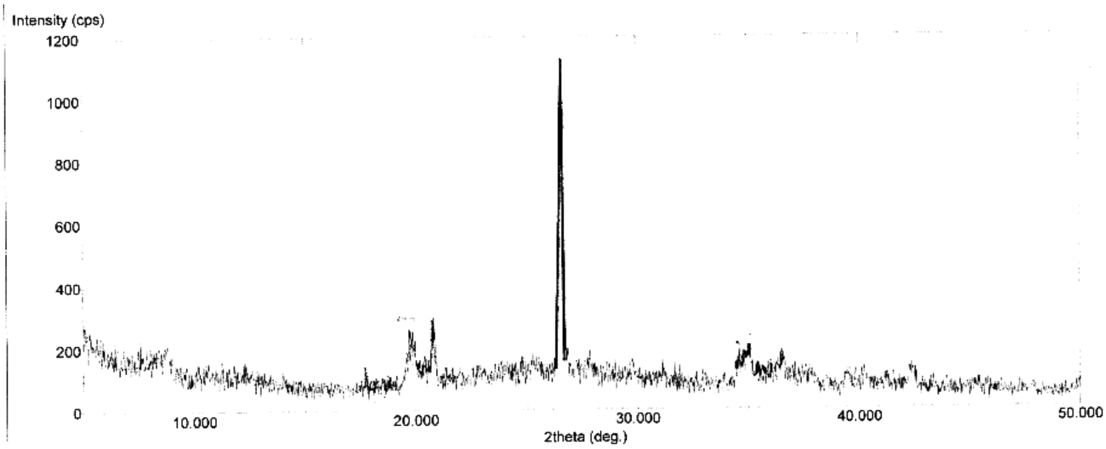


Figure 4.3 XRD pattern of DDM 0.2 (* represent the birnessite peaks)

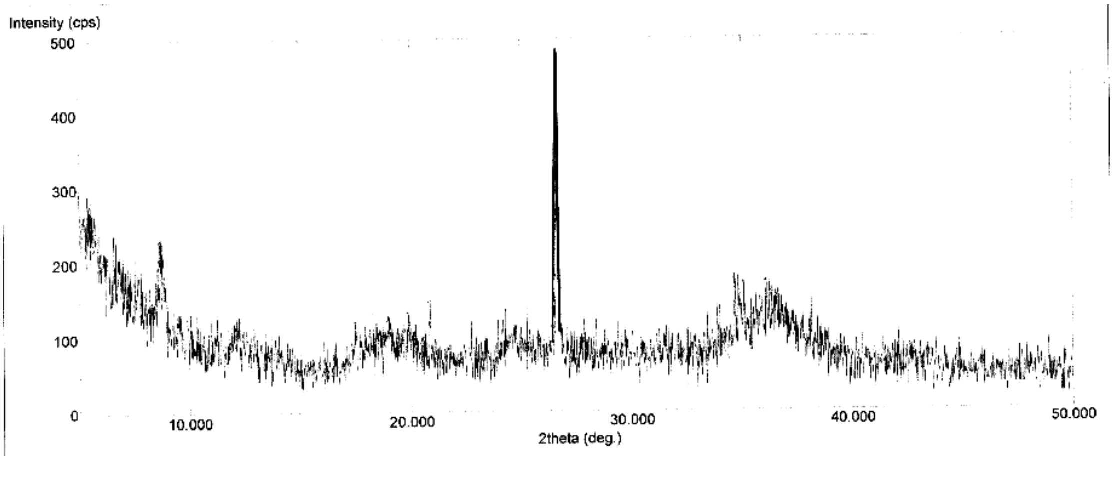


Figure 4.4 XRD pattern of DDM 1.5 (* represent the birnessite peaks)

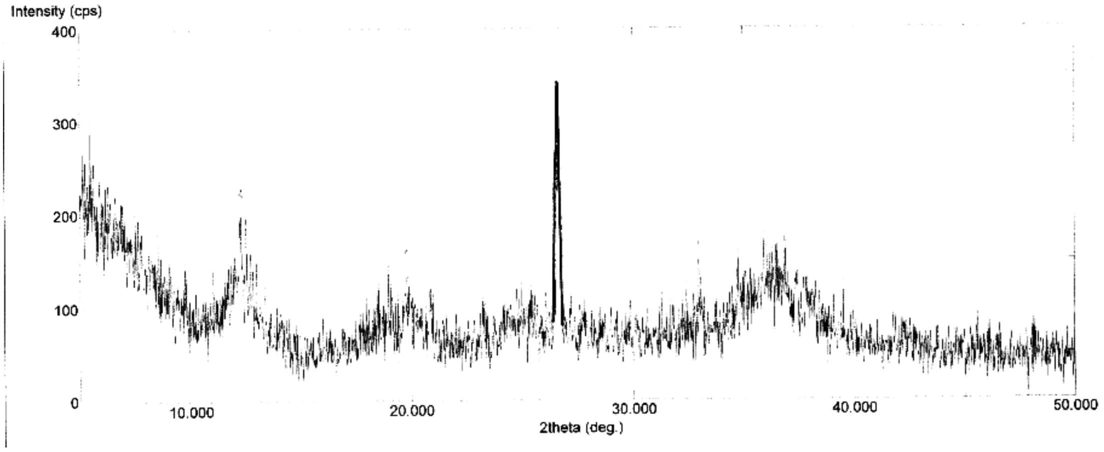


Figure 4.5 XRD pattern of DDM 2.5 (* represent the birnessite peaks)

Figure 4.2 showed XRD patterns of natural diatomite, which consisted the signal at $2\Theta = 26.64^{o}$ corresponding to the SiO_2, which is the main constituent of natural diatomite [32].

Moreover, Figure 4.3-4.5 showed the XRD pattern of DDM 0.2, DDM 1.5, and DDM 2.5. The results showed that, the intensity of signal at $2\Theta = 26.64^{o}$ of natural diatomite has decreased from 2000 to 350 cps after coated with MnO_2. In addition, the important signals (2Θ) of MnO_2 doped onto natural diatomite were 36.24^{o} and 37.30^{o}, which corresponding to other oxide phase and associated with δ-MnO_2 [33]. These signals correspond to birnessite.

4.1.3 By FT-IR

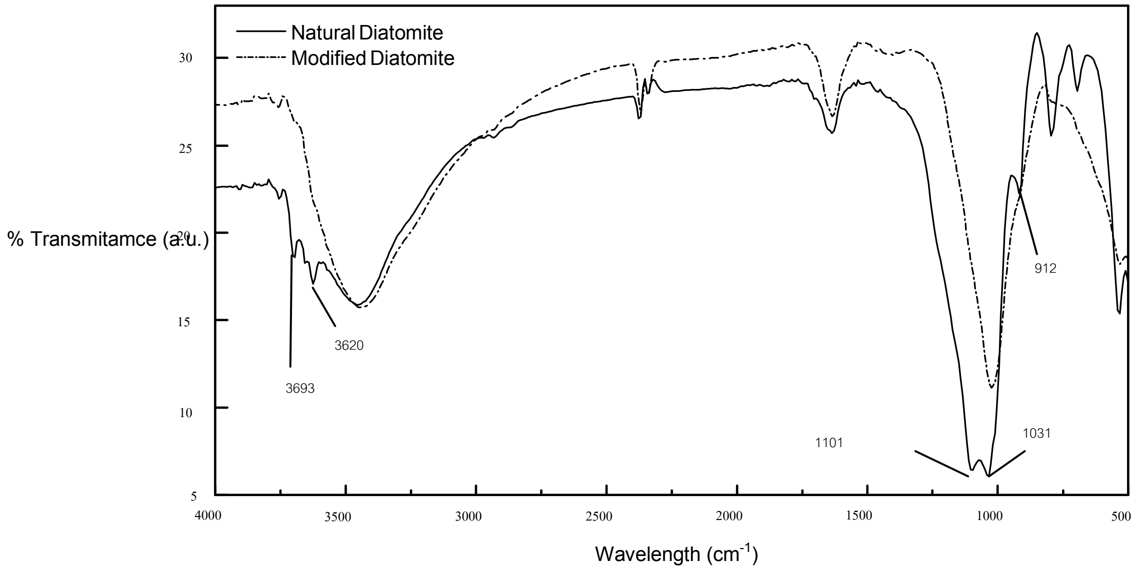


Figure 4.6 FT-IR spectra of natural diatomite and MnO_2 doped diatomite

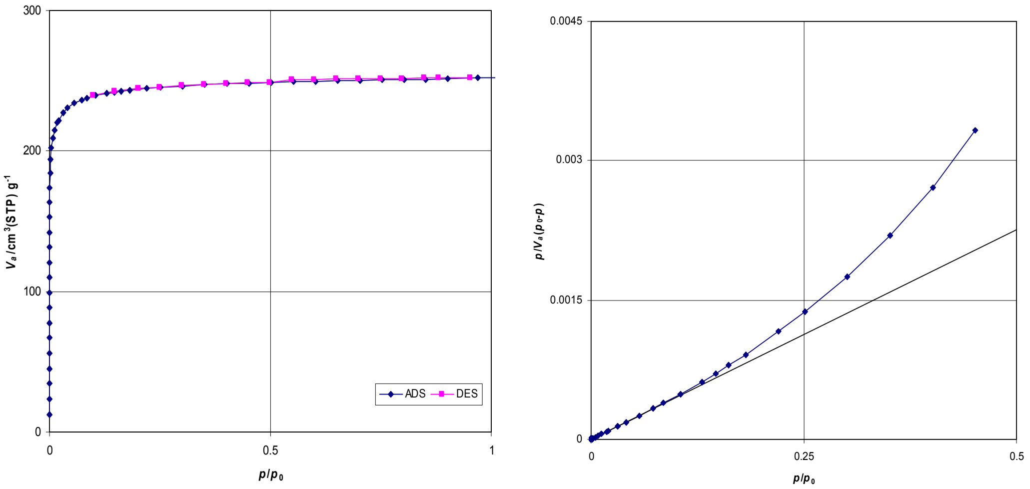
From the analyzed natural diatomite and MnO_2 doped diatomite adsorbent by FT-IR (Figure 4.6), the characteristic peak at 3695, 3620, 1101, 1031, and 912 cm^{-1}. The bands at 3695 and 3620 (weak and narrow) are due to free surface silanal group (Si-OH) , the band at 1101 and 1031 cm^{-1} (strong) are siloxan (Si-O-Si) stretching, while 912 cm^{-1} (weak and broad) band due to (Si-O)stretching of silanol group(Colthup et al., 1990). (11) After modification of natural diatomite the intensity of bands at 3695 and 3620 cm-1 are disappeared since the chemical interactions between the oxides and the surface silinol groups. It could be concluded that the manganese oxides were doped on the surface of natural diatomite.

4.1.4 By Atomic adsorption spectroscopy (AAS)

The amount of manganese oxides doped on the surface of diatomite in which 0.2, 1.5, 2.5 M $MnCl_2$ were 0.0416, 0.1180, and 0.1463 g/g diatomite respectively.

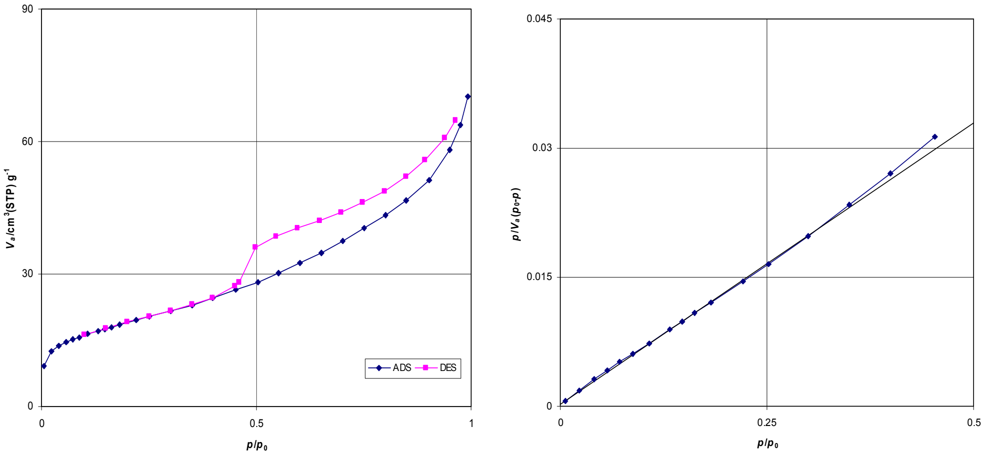
In addition, the amount of manganese oxide loaded on the surface of a support material normally relies on the chemical nature of the material and on the solution acidity duration of treatment (Semushin et al., 1984).

4.1.5 By BET Method



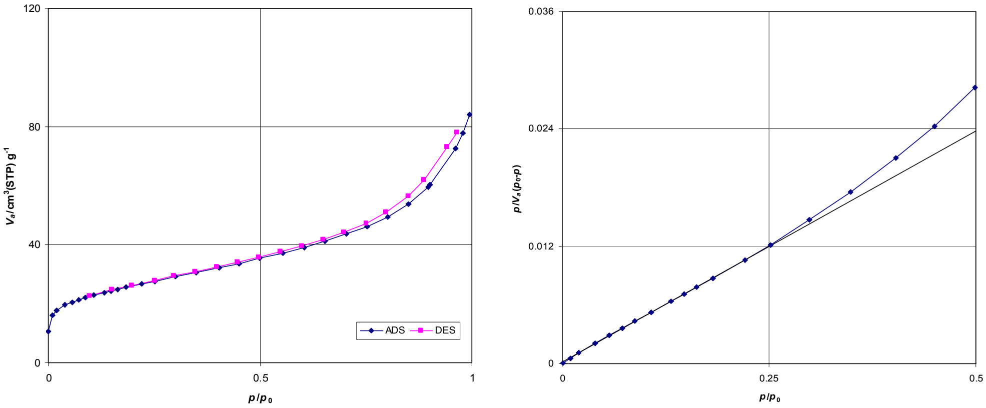
(a) (b)

Figure 4.7 Adsorption/ desorption isotherm and BET plot of Activated charcoal



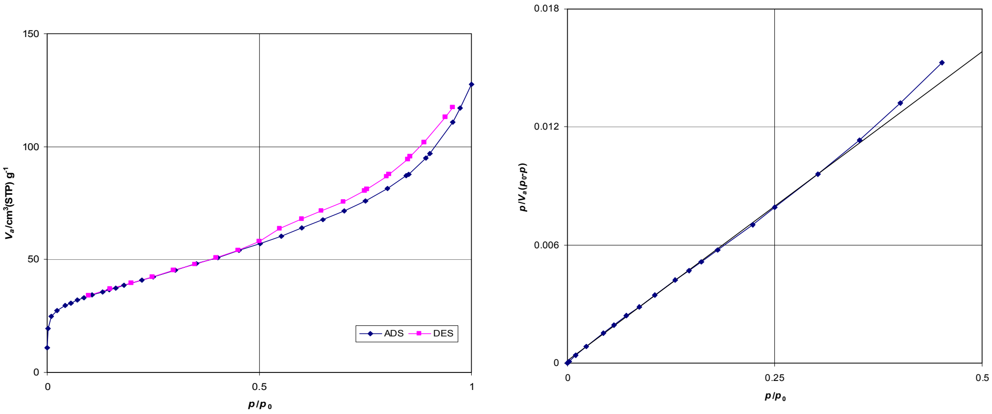
(a) (b)

Figure 4.8 Adsorption/ desorption isotherm (a) and BET plot (b) of natural diatomite



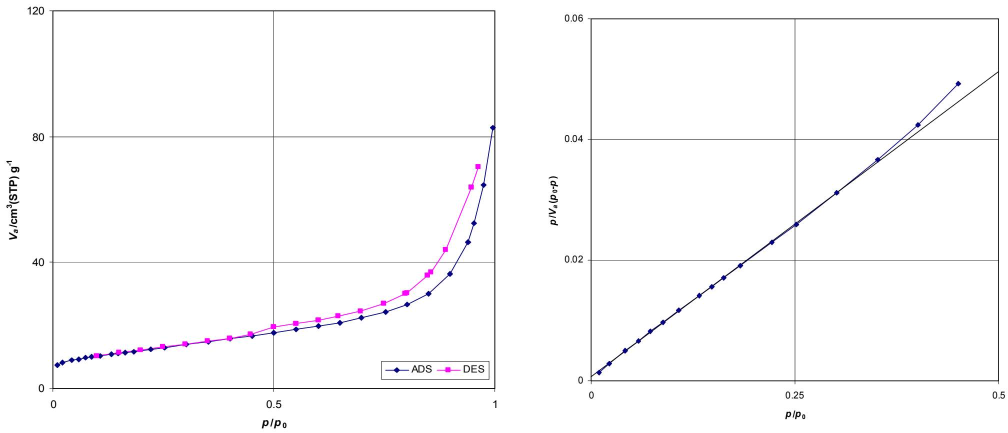
(a) (b)

Figure 4.9 Adsorption/ desorption isotherm (a) and BET plot (b) of DDM 0.2



(a) (b)

Figure 4.10 Adsorption/ desorption isotherm (a) and BET plot (b) of DDM 1.5



(a) **(b)**

Figure 4.11 Adsorption/ desorption isotherm (a) and BET plot (b) of DDM 2.5

Figure 4.7-4.11 and Table 4.1, the surface area of activated charcoal, natural diatomite and DDM 0.2, DDM 1.5, and DDM 2.5 were 967, 66, 92, 138, and 43 m^2/g, respectively. Pore diameter of activated charcoal, natural diatomite and DDM 0.2, DDM 1.5, and DDM 2.5 were 1.6132, 6.4862, 5.5958, 5.5362, and 11.299 nm, respectively. From the obtained data, activated charcoal has high surface area as compare to modified diatomite and natural diatomite. However, pore diameter of activated charcoal was smaller than pore diameter of natural diatomite, DDM 0.2, DDM 1.5, and DDM 2.5.

In addition, adsorption/ desorption isotherm and BET plot from measuring nitrogen adsorption isotherms, a type I, II, IV adsorption isotherm(Table 2.2), Activated charcoal was characterized at Type I which was refer to micropore and activated-Nitrogen, natural diatomite was characterized at Type IV, which was refer to mesopore and silica-Nitrogen. The modified diatomite was characterized at Type II, which was nonporous and oxide-nitrogen.

Table 4.1 Surface area and pore diameter of activated charcoal, natural diatomite DDM 0.2, DDM 1.5, and DDM 2.5

Type of adsorbent	**Surface area (m^2/g)**	**Pore diameter (nm)**
Activated charcoal	967	1.6132
Natural diatomite	66	6.4862
DDM 0.2	92	5.5958
DDM 1.5	138	5.5362
DDM 2.5	43	11.299

From the result of SEM, XRD, FT-IR, AAS, and BET method, it could be concluded that the manganese oxide were doped on the surface of natural diatomite.

4.2 Glycerin purification process

The adsorption of glycerin was by using natural diatomite adsorbent with optimizing various parameters: temperature, contact time, adsorbent dose. In addition, the adsorption process was compared with water washing process.

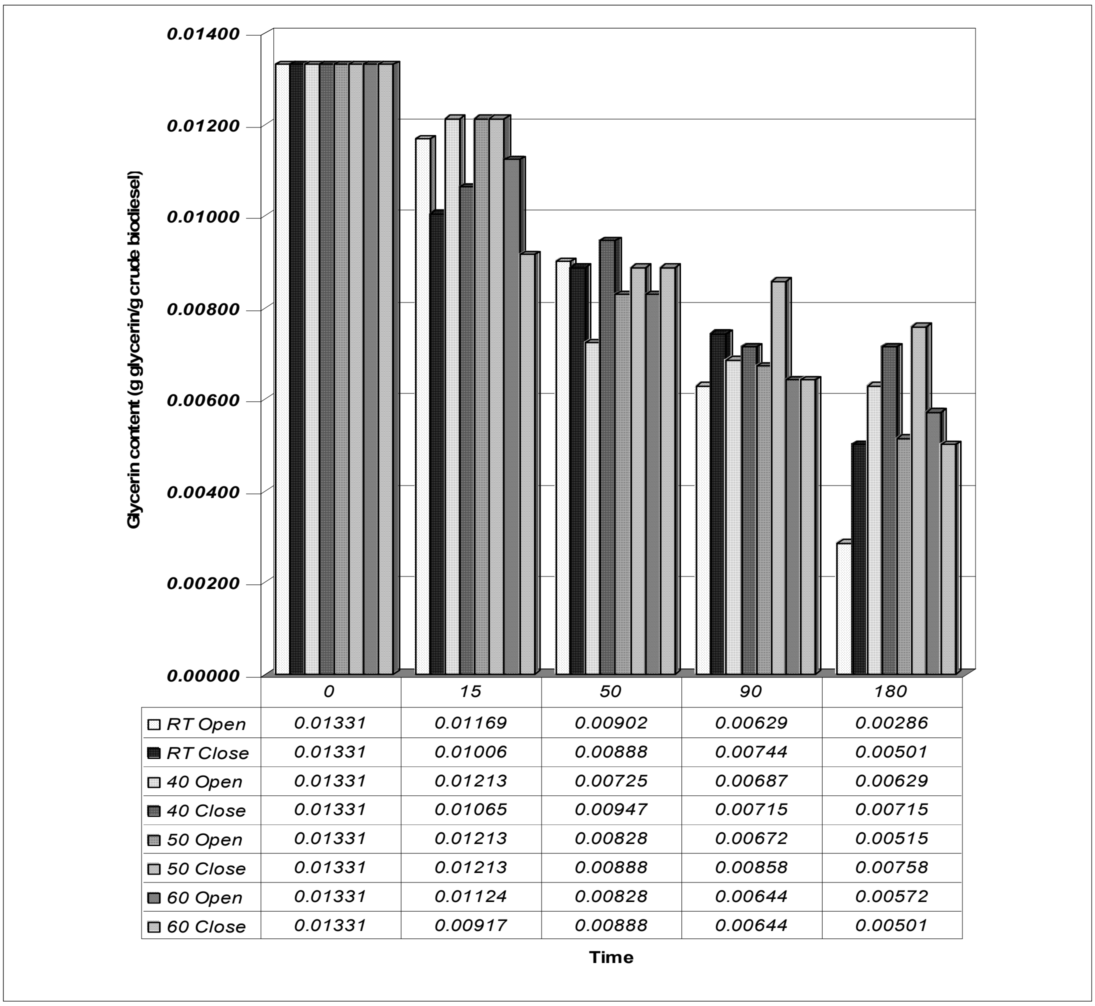
4.2.1 Water-washing process

Table 4.1 and Fig A5 - A6 showed glycerin purification by using water-washing process. The result showed that washed biodiesel with DI water (15x 100) at room temperature, all glycerin was removal and the purified biodiesel met the major specification of biodiesel standards.

Table 4.2 water washing process

Purification process	**biodiesel impurities value**					
	Glycerin (ppm)	**Free glycerol**	**Monoglyceride**	**Diglyceride**	**Triglyceride**	**Total glyceride**
Untreated	4992.16	0.6933	0.4214	0.0367	0	0.8062
Water-washing	0	0	0.4214	0.0367	0	0.1128

4.2.1 Effect of temperature on precipitation of glycerin at various temperatures in close and open systems



Time	0	15	50	90	180
□ RT Open	0.01331	0.01169	0.00902	0.00629	0.00286
■ RT Close	0.01331	0.01006	0.00888	0.00744	0.00501
□ 40 Open	0.01331	0.01213	0.00725	0.00687	0.00629
▨ 40 Close	0.01331	0.01065	0.00947	0.00715	0.00715
▨ 50 Open	0.01331	0.01213	0.00828	0.00672	0.00515
▨ 50 Close	0.01331	0.01213	0.00888	0.00858	0.00758
▨ 60 Open	0.01331	0.01124	0.00828	0.00644	0.00572
▨ 60 Close	0.01331	0.00917	0.00888	0.00644	0.00501

Figure 4.12 Effect of temperature on precipitation of glycerin in close and open systems

When the transesterification reaction was completed, glycerin was gradually separated from biodiesel. Therefore, it is necessary to study the effect of temperature for suspending glycerin in biodiesel during the study of adsorption process.

Figure 4.12 and table B11 showed the effect of temperature on precipitation of glycerin at various temperatures (60 ^{o}C, 50 ^{o}C, 40 ^{o}C, room temperature) in close and open systems. The result showed that after 50 minute the residual glycerin in biodiesel was precipitated from 0.01331 to 0.00888 g glycerin /g crude biodiesel and remained constant at both 50 and 60 °C in close system. Therefore, 50 °C in close system was selected for further study.

4.2.2 Effect of contact time on glycerin adsorption

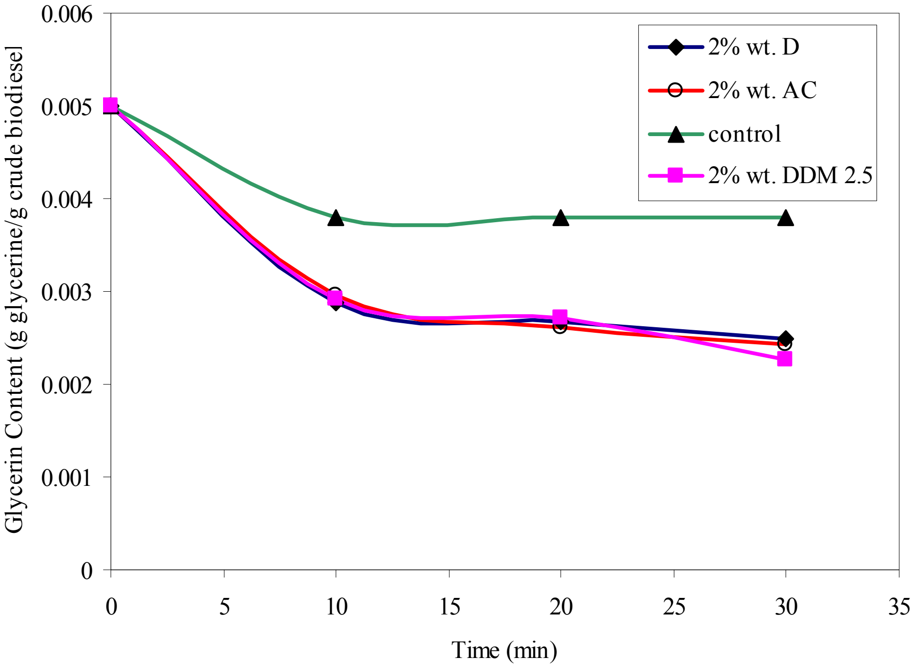


Figure 4.13 Effect of contact time for the adsorption of glycerin onto natural diatomite

For the comparison of efficiency, an activated charcoal was used. The contact time was determined as equilibrium time of 90 %. By using 2 %(w/w) adsorbent, 30 g of crude biodiesel, and stirring rate at 150 rpm for 10-30 min. at 50°C, the concentration of glycerin was decreased from 0.005 to 0.0027 g glycerin/g crude biodiesel. The results were shown in Figure 4.13 and table B 12. The optimum contact time was found to be 20 min.

4.2.3 Effect of concentration of natural diatomite adsorbent for glycerin adsorption (direct treatment)

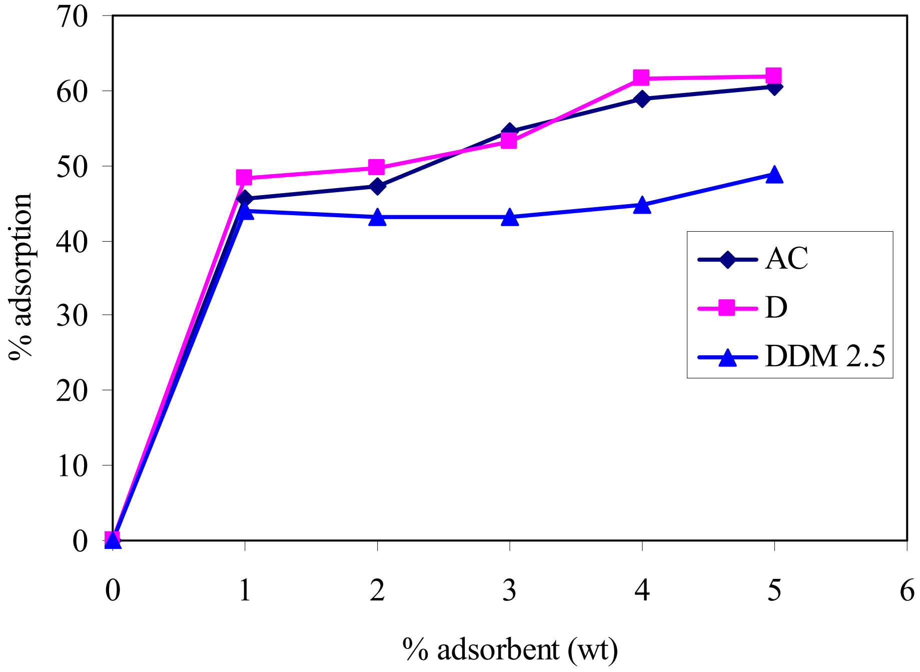


Figure 4.14 Effect of concentration of natural diatomite, Activated charcoal MnO_2 doped diatomite adsorbent for glycerin adsorption

After the biodiesel has been synthesized, the crude biodiesel was subjected to treat with five concentrations of natural diatomite and DDM 2.5 (1, 2, 3, 4, and 5 % wt.) and use activated charcoal as comparison. In 100 ml of glass bottle, 50 g of crude biodiesel was treated at50^{o}C, with stirring rate at 150 rpm and contact time for 20 minutes in water bath (See Figure 4.14). It could be seen that at 4 % wt of natural diatomite and 5% of DDM 2.5 can absorb glycerin up to 61% and 48%. However, the adsorption capacity of DDM 2.5 for glycerin is lower than adsorption capacity of natural diatomite due to porous surface was blocked by MnO_2. In addition, the adsorption capacity of natural diatomite and activated charcoal gave the similar value of adsorption.

4.2.4 Treatment after methanol removal

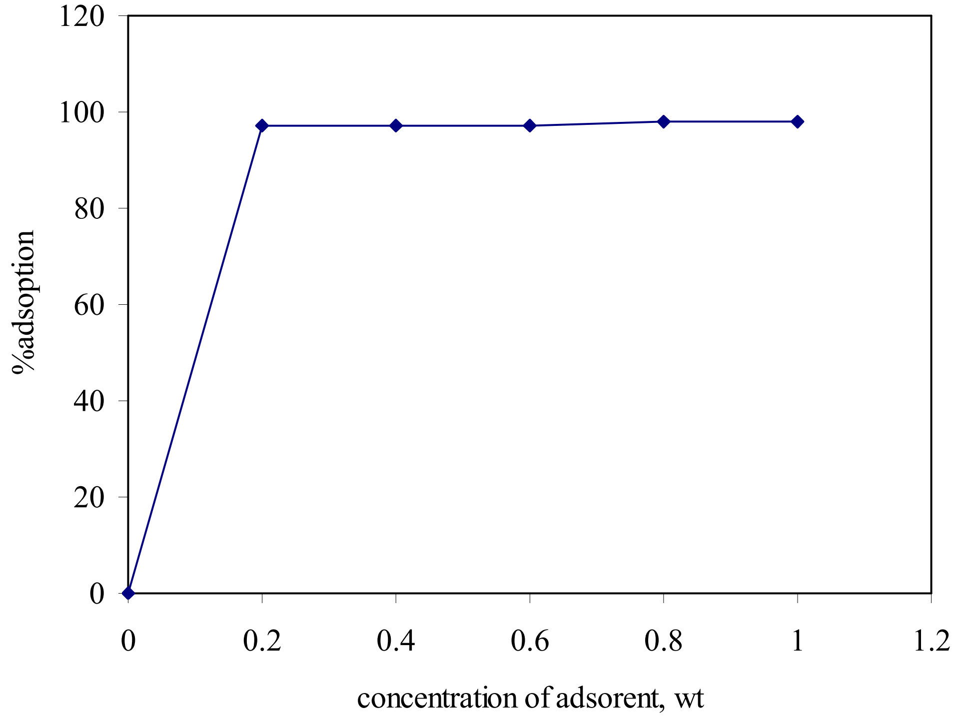


Figure 4.15 Effect of concentration of natural diatomite adsorbent for glycerin Adsorption on methanol removal condition

After the biodiesel has been synthesized, the crude biodiesel was subjected to removal methanol and then treated with five concentrations of natural diatomite (0.2, 0.4, 0.6, 0.8 and 1 %wt.) In a 100 mL of glass bottle, 50 g of crude biodiesel was treated with natural diatomite adsorbent at 50°C, with stirring rate at 150 rpm and contact time for 20 minutes in water bath. The percent adsorption was increased up to 98 % by using 1 % of natural diatomite as showed in figure 4.15, A 8 and table B14. 12 hours after treatment, the purification of glycerin in biodiesel has been observed, when 0.2-0.8 % wt. of adsorbent was used, while 1% wt. of adsorbent gave the clear solution of biodiesel. Therefore 1% of adsorbent could be used to absorb glycerin in this process.

From the result of 4.2.3 and 4.2.4, it could be concluded that the efficiency of adsorption could be affected by methanol. Therefore the methanol must be removed before the glycerin was treated by adsorbent.

4.3 Breakthrough point and capacity of natural diatomite for glycerine adsorption

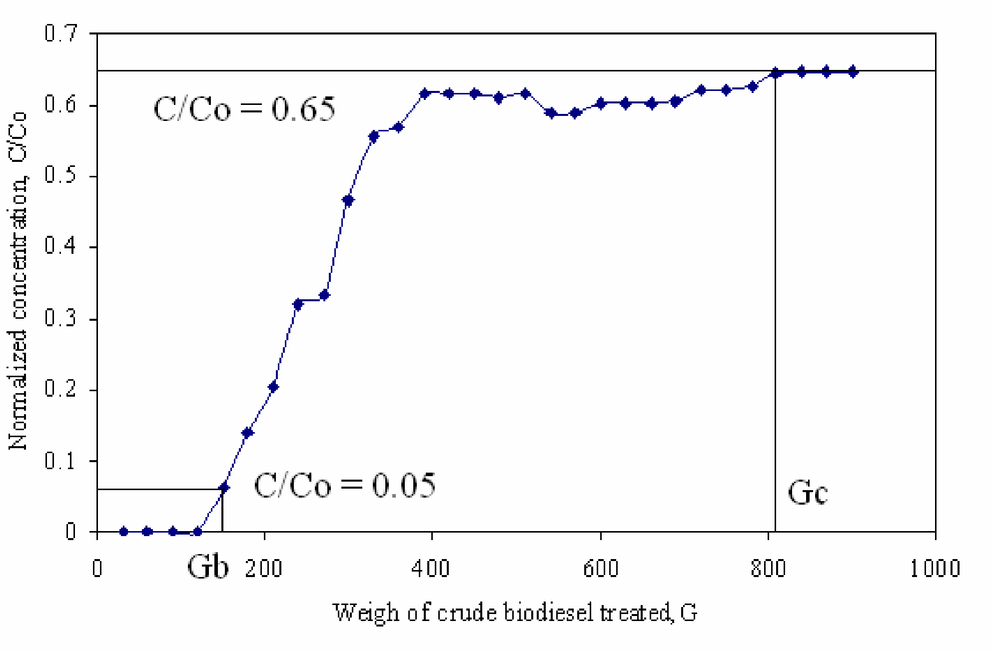


Figure 4.16 Breakthrough and capacity of natural diatomite for glycerin adsorption

According to Figure 4.16 and Table B 15, by treating biodiesel (30x30g) with natural diatomite (1g) at 50 ^{o} C and stirring rate150 rpm for 10 minutes, the break though point was reached at 5% of the influent concentration (Gb=150g), the capacity of adsorbent was reached at 95% of effluent concentration (Gc= 810 g).

Therefore, breakthrough point and capacity of natural diatomite onto glycerin adsorption were 145.85 mg/g and 2420.62 mg/g, respectively.

4.4 Adsorption isotherm of glycerin

Ten concentrations of adsorbent: 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 %wt were studied. 30 g of crude biodiesel was treated with each adsorbent at 50 ^{o}C, with stirring rate at 150 rpm for 20 minutes. Based on data, Langmuir and Freundlich isotherms were obtained for glycerin as showed in figures 4.17, 4.18 and table B 16. The calculated langmuir and freundlish parameter are reported in Table 4.3.

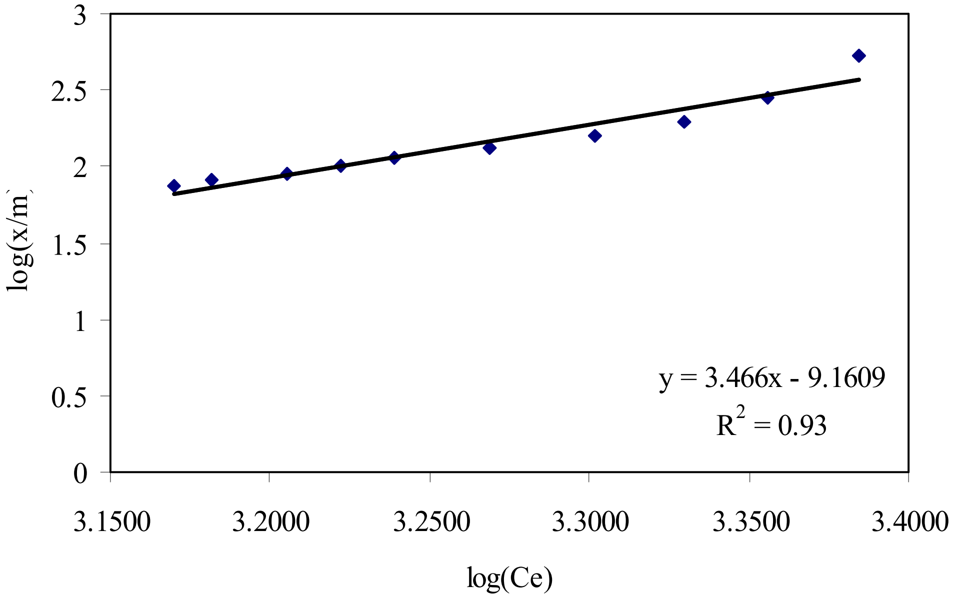


Figure 4.17 Freundlich adsorption isotherm for glycerin

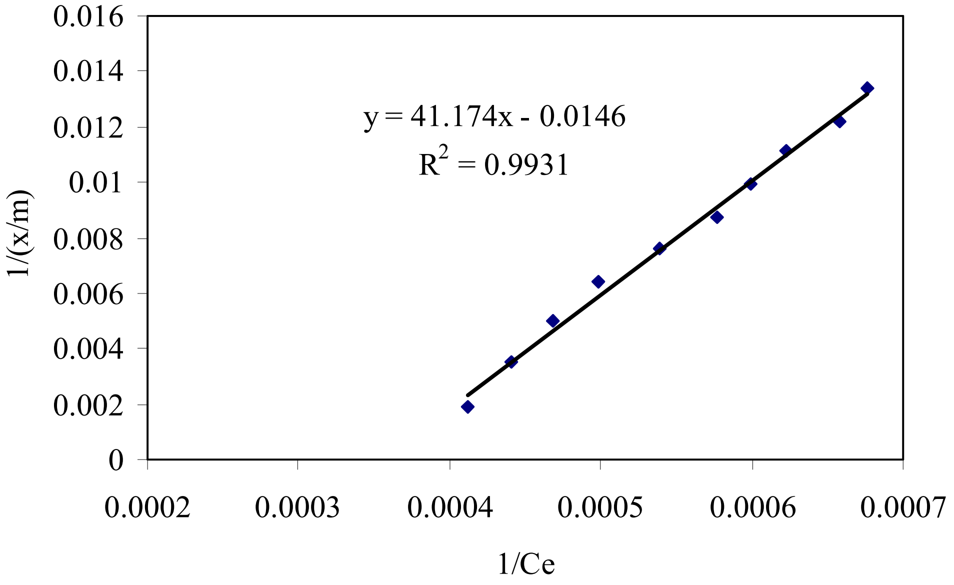


Figure 4.18 Langmuir adsorption isotherm for glycerin

Table 4.3 Langmuir and Freundlich isotherm constant for adsorption glycerin onto natural diatomite

Adsorbate	Fruendlich isotherm				Langmuie isotherm			
Glycerin	Intercept log K_f (l/g)	K_f (l/g)	slope 1/n	R^2	a (mg/g)	b (l/mg)	R^2	R_L*
	-9.1609	6.91*10^-10	3.466	0.9932	68.493	3.54*10^-4	0.9931	0.3721

** Example for Rl calculation sees in appendices c*

Table4.3 showed coefficient of Freundlish isotherm is close to Langmuir isotherm, therefore the adsorption isotherm of glycerin was physisorption and chemisorption. The maximum adsorption capacity (a) and empirical constant (K_f) of natural diatomite for glycerin removal were 68.493 mg/g and 6.91*10^-10 (l/mg). According to the R_L values in Table 2.2, the adsorption behavior of glycerin is favourable ($R_L<1$).

4.5 Monoglyceride purification process

The adsorption of monoglyceride was studies by using difference types of adsorbent with optimizing various parameters: contact time, adsorbent dosage, and effect of $MnCl_2$ concentration doped on natural diatomite. The biodiesel used in this study was so called "treated biodiesel" which was subjected to purify by adsorption process and water-washing process.

4.5.1 Comparison of various types of adsorbent on adsorption of monoglyceride

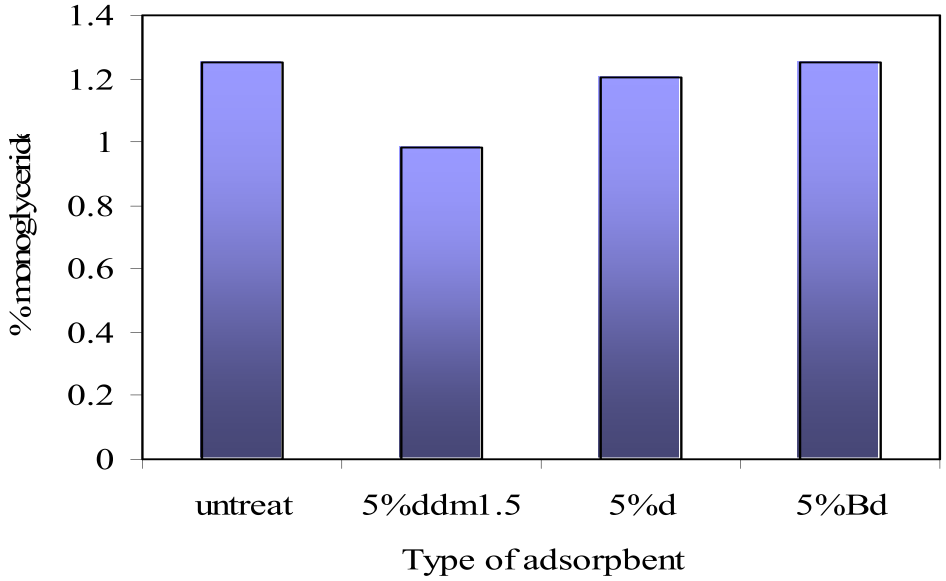


Figure 4.19 Comparison of various types of adsorbents on adsorption of monoglyceride

The comparison of various types of adsorbent, natural diatomite, DDM1.5, and calcined diatomite were studied by using optimum condition at 50^{o}C, stirring rate at 150 rpm for 10 minutes. The result showed that DDM 1.5 gave the best result on monoglyceride removal as showed in Figure 4.19.

4.5.2 Effect of contact time for the adsorption of monoglyceride with MnO_2 doped diatomite

The equilibrium time of 90 % adsorption of the adsorbed (monoglyceride) amount was calculated as contact time. Figure 4.20, A9-A13 and Table 17 showed the effect of contact time for the adsorption of monoglyceride with MnO_2 doped diatomite, by treating 10 g of treated biodiesel with 5%wt. of DDM 1.5 at 50^{o}C and stirring rate at 150 rpm with various contact times (5, 10, 15 and 20 minute).The result showed that percent of monoglyceride content was decreased from 1.25 to 0.98 % (m/m) and remained constant after at 10 minutes. Therefore, the optimum contact time was found to be 10 minutes.

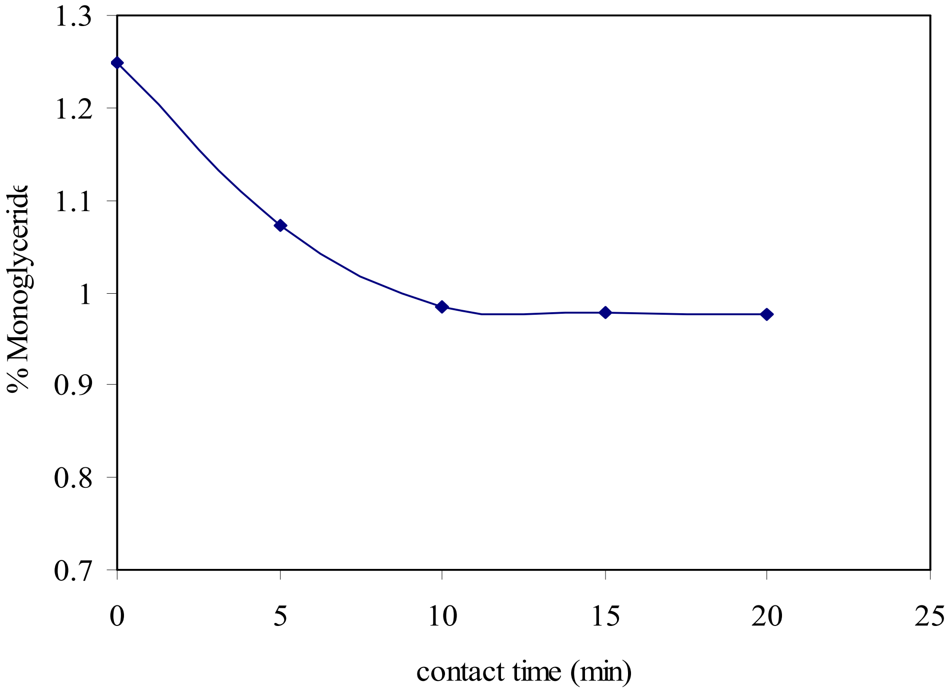


Figure 4.20 Effect of contact time for the adsorption of monoglyceride with MnO_2 doped diatomite

4.5.3 Effect of $MnCl_2$ concentration doped on natural diatomite for monoglyceride removal

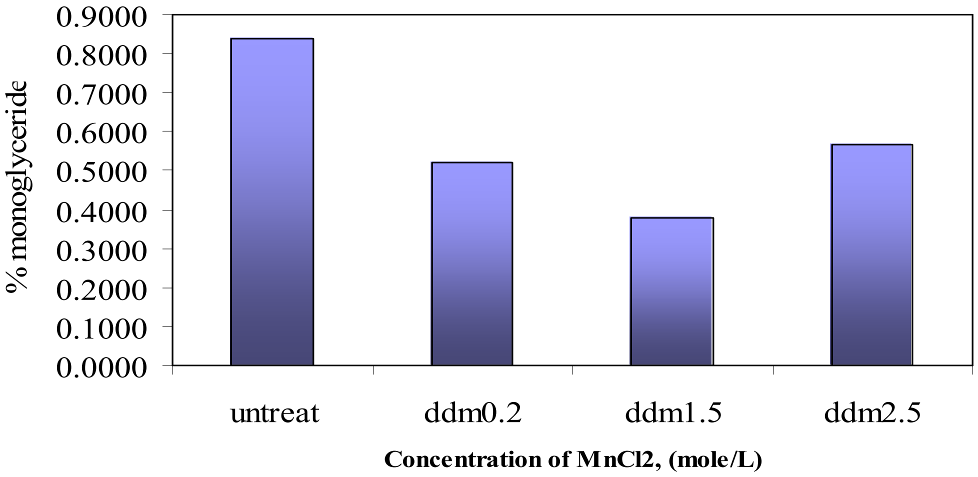


Figure 4.21 Effect of concentration of $MnCl_2$ (mole/L) doped on natural diatomite for monoglyceride removal

By treating treated biodiesel (10 g) with 5 % wt of different manganese oxide doped diatomite (0.2M, 1.5M, and 2.5M), at 50°C with stirring rate at 150 for 10 minutes, the result showed that % monoglyceride was reduced from 0.83 to 0.51, 0.38, and 0.56 %, respectively, with 28.92 % of monoglyceride could be removed by DDM 1.5 as showed in Figure 4.21, A26-A28 and Table B 20.

4.5.4 Effect of concentration of DDM 1.5 for monoglyceride removal

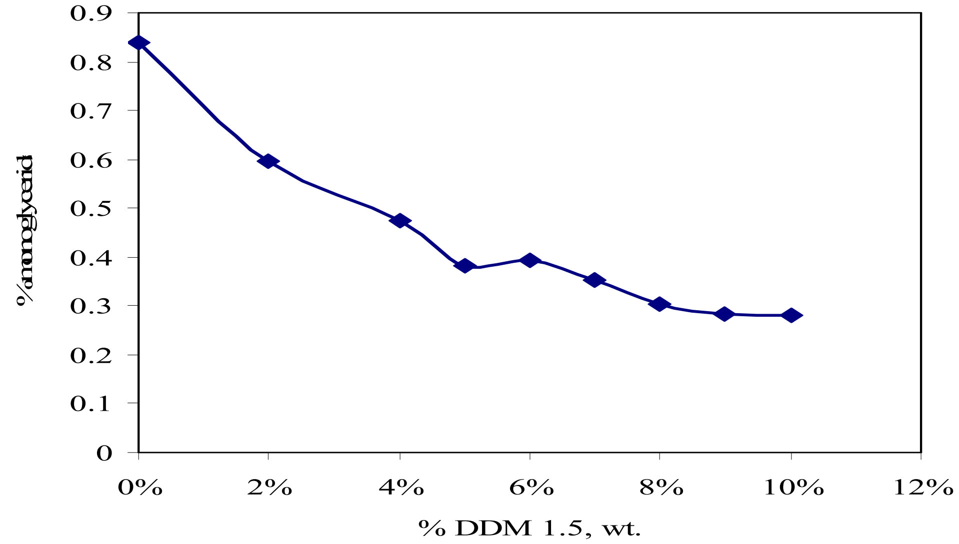


Figure 4.22 Effect of concentration of modified diatomite adsorbent for monoglyceride removal

The effect of concentration of DDM 1.5 for monoglyceride removal was shown in Figure 4.22, A17-A25 and Table B 19. The result showed that at least 2% of DDM 1.5 could be reduced % monoglyceride content down to requited standard for biodiesel. The percentage of monoglyceride content was decreased from 0.83 to 0.59 % (m/m) at 50°C with stirring rate at 150 rpm and contact time at 10 minutes in water bath and the percent adsorption of monoglyceride onto 2% DDM 1.5 was 28.9%. In addition, % monoglyceride content in biodiesel depends on temperature of biodiesel synthesis, If using more than 70°C for synthesis biodiesel, %(m/m) monoglyceride content would be highs value.

4.6 Adsorption isotherm of monoglyceride

Seven concentrations of adsorbent: 2, 5, 6, 7, 8, 9, and 10 %wt were studied. In a 100 mL glass bottom, 10 g of treated biodiesel was treated with DDM 1.5 at 50 °C, with stirring rate at 150 rpm for 10minutes in water bath. Based on data, Langmuir and Freundlish isotherms were obtained for monoglyceride as showed in figures 4.23-4.24, A17-A25, and B21. The calculated langmuir and freundlish parameters were reported in Table 4.4.

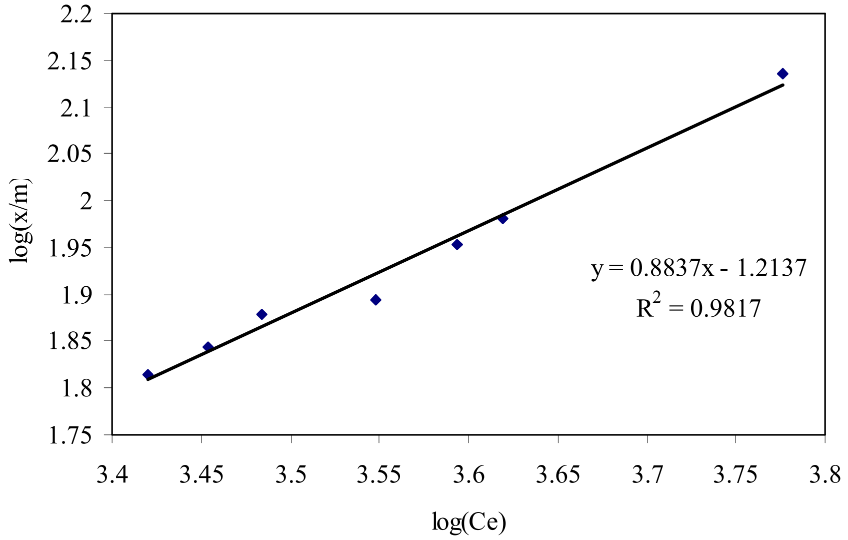


Figure 4.23 Freundlishr adsorption isotherm for monomonoglyceride

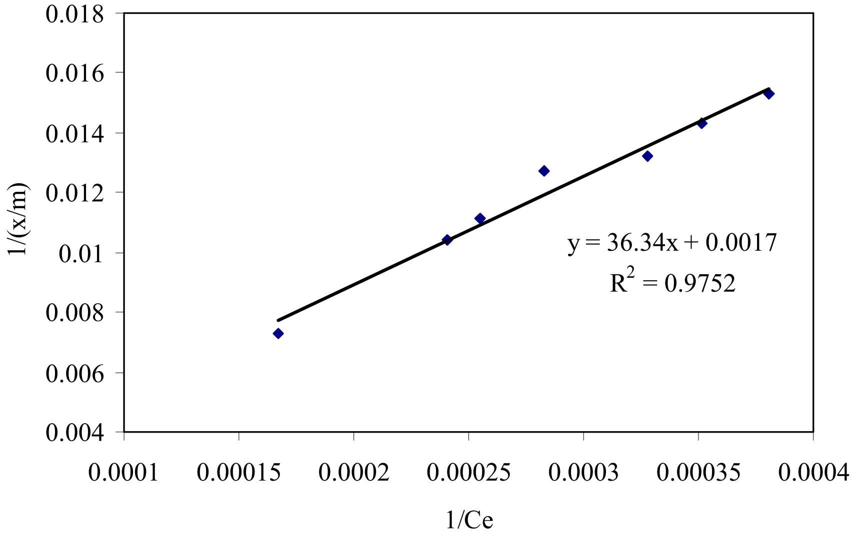


Figure 4.24 Langmuir adsorption isotherm for monoglyceride

Table 4.4 Langmuir and Freundlish isotherm constants for adsorption monoglyceride onto DDM 1.5.

Adsorbate	Freundlich parameters				Langmuir parameters			
Monoglyceride	Intercept logKf	K_f (l/g)	slope 1/n	R^2	a (mg/g)	b (l/mg)	R^2	R_L
	-1.2137	0.0611	0.8837	0.9817	588.23	0.04678 *10^-3	0.9752	0.7184

Table 4.4 showed coefficient of Freundlich isotherm was closed to Langmuir isotherm, therefore the adsorption isotherm was physisorption and chemisorption. The maximum adsorption capacity (a) and empirical constant (K_f) of natural diatomite for monoglyceride removal were 588.23 mg/g and 0.0611 (l/g). According to the R_L values in table 2.2, the adsorption behavior of glycerin is favourable ($R_L<1$) and tend to be linear.

4.7 Properties of treated biodiesel

The some properties (i.e. viscosity, flash point, acid value,and density) of treated biodiesel were determined. The results were shown in table 4.5.

Table 4.5 Properties of treated biodiesel

Property	Biodiesel's value		Standard' s value	Method
	with dry-washing	with water-washing		
Viscosity at 40 °C (mm^2/s)	4.2	4.24	3-5 mm^2/s	ASTM D445
Flash point (°C)	>120	>120 °C	>120 °C	ASTM D93

Table 4.5 Properties of treated biodiesel (continuous)

Property	**Biodiesel's value**		**Standard' s value**	**Method**
	with dry-washing	**with water-washing**		
Acid number (mg KOH/g)	0.0673	0.0671	< 0.5 mg KOH/g	ASTM D974
Free glycerol	0.011	0	<0.02	EN 14105
Monoglyceride %wt.	0.42	0.34	<0.80	EN 14105
Diglyceride %wt.	0.037	0.038	<0.20	EN 14105
Triglyceride %wt.	0	0	<0.20	EN 14105
Total glyceride %wt.	0.12	0.094	<0.25	EN 14105

It could be seen in Table 4.5 that the properties of treated biodiesel were in rang of biodiesel standards. Therefore, the adsorption process using natural diatomite adsorbent could be used to purify biodiesel in place of water-washing process.

ECONOMIC POINT OF VIEW

Table 1 Estimate cost of biodiesel purification process of 1 kg biodiesel

Water washing				
Electrical cost	**Electrical power (kw)**	**time used (min)**	**electricity used (unites)**	**Electricity charge * (B)**
Evaporation	0.414/h	60	0.414	1.088
Stirring	1/h	20min. x 5	0.333 x 5	4.379
Material cost	**Amount used (L)**	**Cost per unit(B)**		**Value (B)**
water	5	**15Baht/m^3		0.075 Baht
Total cost of water-washing treatment				5.542baht/kg
Cost of waste water treatment 30 – 80 baht /m^3				
Dry washing for glycerin(D)				
Electrical cost	**Electrical power (kw)**	**time used (min)**	**electricity used (unites)**	**Electricity charge * (B)**
Stirring	1/h	20	0.333	0.876
Material cost	**Amount used**	**Cost per unit**		**Value (B)**
natural diatomite	10 G	2Baht/kg		0.02
Total cost of natural diatomite treatment				0.89baht/kg
Return cost from sell used natural diatomite 1-2 baht/kg				

**2.63 Baht/unite (According to the electricity tariff application any government and agency (12 kv and low), 2010)*

***15Baht/m^3 (According to the Provincial Waterworks Authority, State Enterprise,Industrial and large Business)*

The cost of water-washing process is mainly depending on the cost of stirring and water used for the removal of glycerin from crude biodiesel. The total cost of water-washing was about 5.542 baht/kg. After water-washing process, generated waste water could be treated and the cost of waste water treatment was about 30 – 80 baht /m^3. Moreover, the cost of reactor of waste water treatment could be included.

The cost of a dry-washing process is mainly depending on the cost of the natural diatomite adsorbent used and electricity of stirring for the removal of glycerin from crude biodiesel. The total cost of natural diatomite treatment was about 0.89 baht/kg. After natural diatomite was used to purify biodiesel, it could be sold to factory of cement and the return cost was about 1-2 baht/kg.

. From the Table 1, it could be seen that the cost of purification biodiesel by using natural diatomite is lower when compared with the cost of using water-washing process.

CHARPTER V

CONCLUSION

Low cost natural diatomite could be used as adsorbent for purifying biodiesel in dry-washing process as it has capacity to adsorb glycerin in biodiesel as well as activated charcoal. The glycerin adsorption process was studied by optimizing various parameters: temperature, contact time, adsorbent concentration. In addition, the effect of methanol contained in crude biodiesel onto adsorption process was also studied. The results showed that, by using 4 % (w/w) of adsorbent at 50 ^{o}C with stirring rate 150 rpm for 20 minutes, the level of total glycerin was lower than of the specification of biodiesel standard (< 0.25%wt). However, 98% of glycerin was removed by using 1% (w/w) of D adsorbent on the condition that methanol had been removed before treatment. Adsorption capacity and breakthrough values were 2420.62 mg/g and 145.85 mg/g, respectively. According to the adsorption isotherm, this process is fit to both Fureundlich and Langmuir models.

Moreover, the monoglyceride adsorption process was studied by optimizing various parameters: contact time, adsorbent concentration, types of adsorbents, and effect of initial $MnCl_2$ concentrations doped on natural diatomite. It could be concluded that, by using 2% (w/w) of DDM 1.5 adsorbent at 50^{o}C with stirring rate 150 rpm for 10 minutes, 28.92 % of monoglyceride could be removed. In addition, the diatomite doped with 1.5M $MnCl_2$ gave the best removal efficiency for monoglyceride. According to the adsorption isotherm, this process is fit to both Fureundlich and Langmuir models.

Finally, this adsorption 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. The advantage over conventional water washing process is no wastewater generated from this adsorption process.

SUGGESTION

Following recommendations are suggested for future research:

1. New type and particle size of adsorbents for glycerin removal.
2. New type of supports for doping with MnO_2.
3. Other types of doping material.

REFERENCES

[1] Schuchardf, U., Sercheli, R. and Vargas, R.M. Transesterification of vegetableoils: a review. Journal of the Brazilian Chemical Society 9 (1998): 199-210.

[2] Kumar, S., Gupta, A.K. and Naik, S. Conversion of non-edible oil into biodiesel. Journal of Scientific and Industrial Research 62 (2003): 124-132.

[3] Marchetti J.M., Miguel V.U., Errazu A.F.. Possible methods for biodiesel production. Renew. Sust. Energy Rev. 11 (2007):1300–1311.

[4] Freedman B., Butterfield R.O. and Pryde EH. Transesterification kinetics of soybean oil. J. Am. Oil. Chem. Soc. 63 (1986): 1375–1380.

[5] Moore, W. S. and D. F. Reid Extraction of radium from natural waters using manganese-impregnated acrylic fibers. J. Geophys. Res. 78 (1973): 8880 – 8886.

[6] Moslehi P., Nahid P., Heavy metal removal from water and wastewater using raw and modified diatomite. IJB Transactions B 29 (2007) : 141-146.

[7] Maskan M., Bagci H. Effect of different adsorbents on purification of used sunflower seed oil utilized for frying. Eur Food Res Technol 217 (2003): 215– 218.

[8] Ahmad, A.L., Bhatia, S., Ibrahim, N. and Sumathi, S. Adsorption of residual oil from palm oil mill effluent using rubber powder. *Brazillian* Journal of Chemical Engineering 22 (2005): 371-379.

[9] Bertram, B., Abrams, C. and Cooke, B.S. Purification of biodiesel with adsorbent materials. U.S. Patent Application No.20050081436, 2005.

[10] Metcalf & EDDY,Inc Wastewater Engineering Treatment Disposal and Reuse (3 ed). MCGRAW Hill: NY. 1991.

[11] Gregg, S.J. & Sing, K.S.W., Adsorption Surface Area and Porosity, (2 Ed). Academic Press INC: London, 1998.

[12] Rouquerol, F., Rouquerol, J. & Sing, K.S.W., Adsorption by Powders and Porous Solids. Academic Press INC: London, 1999.

[13] ประกาศกรมธุรกิจพลังงาน เรื่อง กำหนดลักษณะและคุณภาพของไบโอดีเซลประเภทเมทิล-เอสเทอร์ของกรดไขมัน. *ราชกิจจานุเบกษา* ตอนพิเศษ 70 ง (2548): 122

[14] Mustranta, A., Forssell, P. and Poutanen, K. Application of immobilized lipase to transesterification and esterification reaction in nonaqueous systems. Enzyme and Microbial Technology 15 (1993): 133-139.

[15] Fukuda, H., Kondo, A. and Noda, H. Biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering 92 (2001): 405-416.

[16] Freedman B., Butterfield R.O. and Pryde EH. Transesterification kinetics of soybean oil. J. Am. Oil. Chem. Soc. 63 (1986): 1375–1380.

[17] Madras, G., Kolluru, C. and Kumar, R. Synthesis of biodiesel in supercritical fluids. Fuel 83 (2004): 2029-2033.

[18] Axens IFP Group Technologies, Activated Alumina & Molecular Sieves Quality and advanced technology. Rueil-Malmaison Cedex: France, 2002.

[19] Al Degs Y., Khraisheh M. A. M., Tutunji M. F. Sorption of lead ions on diatomite and manganese oxides modified diatomite. Water Res. 35(2001): 3724-3728.

[20] Berriosa M., Skeltonb R.L. Comparison of purification methods for biodiesel. Chem. Eng. J.144 (2008): 459–465

[21] Majeda A.M. Khraisheh , Yahya S. Al-degs , Wendy A.M. Mcminn. Remediation of wastewater containing heavy metalsusing raw and modified diatomite. Chem. Eng. J. 99 (2004): 177–184.

[22] Oliveira M. B., Varanda F. R., Marrucho I. M., Queimada A. J., and Coutinho J. A. P.. Prediction of water solubility in biodiesel with the CPA equation of State. Ind.Eng. Chem. Res. 47 (2008): 4278–4285.

[23] Moˆnica C.G. Albuquerque, et al., MgM (M = Al and Ca) oxides as basic catalysts in transesterification processes. Applied Catalysis A: General 347 (2008): 162–168.

[24] Bryan T., Adsorbing it all. Biodiesel magazine (2005): 40-43.

[25] Allen S.J., Brown P.A., J. Competitive sorption of copper and nickel ions from aqueous solution using peat. Chem. Technology & Biotechnology 62 (1995): 17.

[26] Al-Degs Y.S., Khraisheh M.A.M., Allen S.J., Ahmad M.N., Effect of carbon on the removal of reactive dyes from textile effluent. Water Research. 34 (2000): 927.

[27] Panday K.K., Prasad G., Singh V.N., Copper (II) removal from aqueous solution by fly ash. Water Research 19 (1985): 869.

[28] Van Gerpen J., Shanks B., Pruszko R., Biodiesel Analytical Methods. NREL: USA, 2004

[29] Xiangying Zeng, Er Li, and Yuehua Fan, Removal of chromium ion (III) from aqueous solution by manganese oxide and microemulsion modified diatomite. Journal of hazardous materials 238 (2006) : 158-165

[30] Yehya S., Al-Degs, Majeda A.M., Mohammad N.A., Mechanisms and chemistry of dry adsorption on manganese oxides-modified diatomite. Journal of environtal mangagement 90 (2009): 3520-3527.

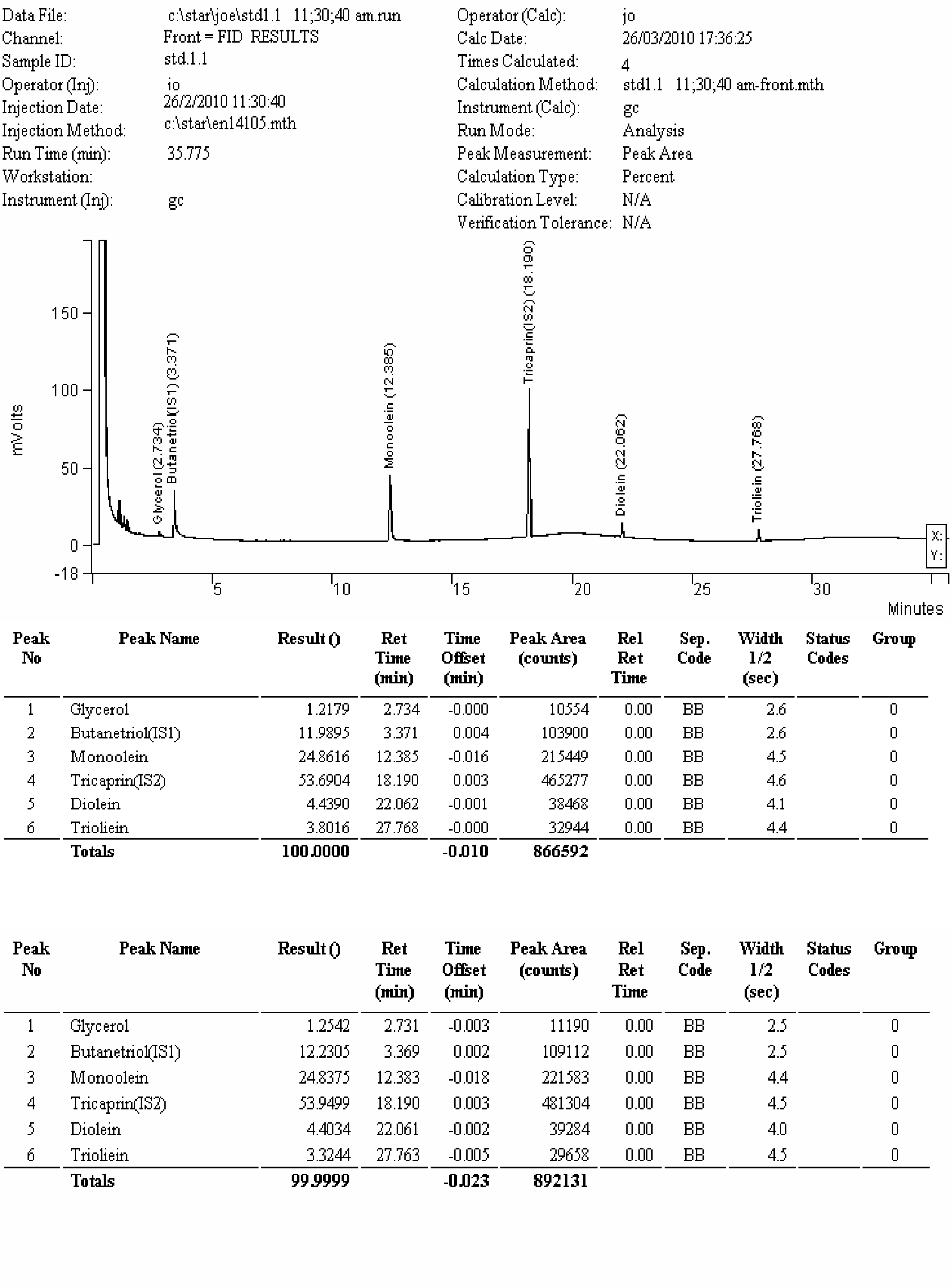
[31] Xiangying Zeng Er Li, and Yuehua Fan, Removal of chromium ion (III) from aqueous solution by manganese oxide and microemulsion modified diatomite. Journal of environtal mangagement 238 (2009): 158-165

[32] Apiratikul, R. Sorption of heavy meals by green macro alga, caulerpa lentillifera and modified zeolite from coal fly ash. Doctoral Dissertation Field of Study Environmental Management Graduate School, Chulalongkorn University, 2006.

[33] Huang, K.C., Hoaga, G.E., Chheda, P., Woody, B.A., Dobbs, M.G., Chemical oxidation of trichloroethylene with potassium permanganate in a porous medium, Advances in Environmental Research 7, (2002): 217–229.

APPENDICES

APPENDIX A



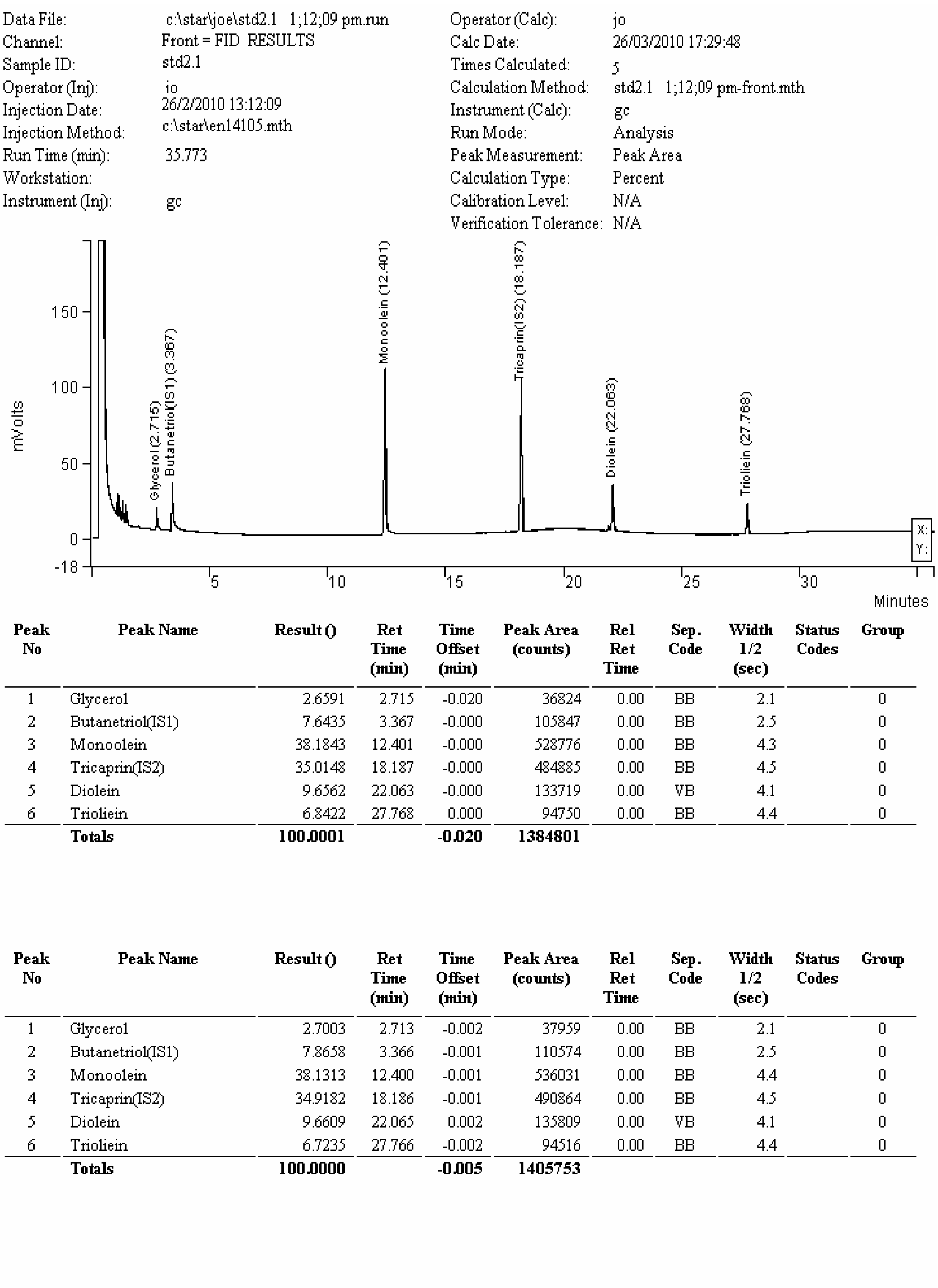
Data File: c:\star\joe\std1.1 11;30;40 am.run
Channel: Front = FID RESULTS
Sample ID: std.1.1
Operator (Inj): io
Injection Date: 26/2/2010 11:30:40
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 26/03/2010 17:36:25
Times Calculated: 4
Calculation Method: std1.1 11;30;40 am-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Triolein	3.8016	27.768	-0.000	32944	0.00	BB	4.4		0
	Totals	**100.0000**		**-0.010**	**866592**					

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	Triolein	3.3244	27.763	-0.005	29658	0.00	BB	4.5		0
	Totals	**99.9999**		**-0.023**	**892131**					

Figure A1 GC chromatogram of Standard 1.



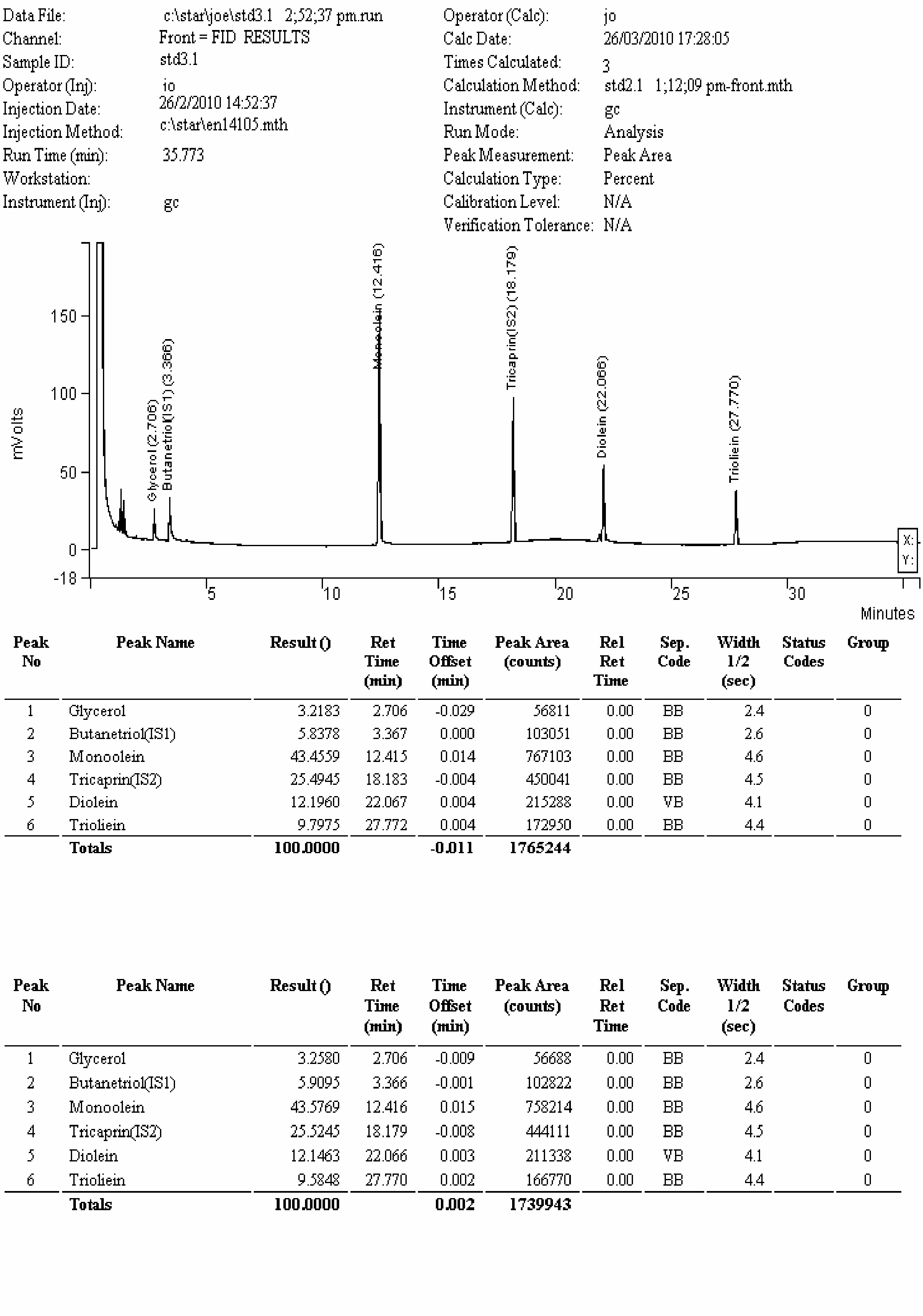
Data File: c:\star\joe\std2.1 1;12;09 pm.run
Channel: Front = FID RESULTS
Sample ID: std2.1
Operator (Inj): io
Injection Date: 26/2/2010 13:12:09
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 26/03/2010 17:29:48
Times Calculated: 5
Calculation Method: std2.1 1;12;09 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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**					

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 A2 GC chromatogram of Standard 2



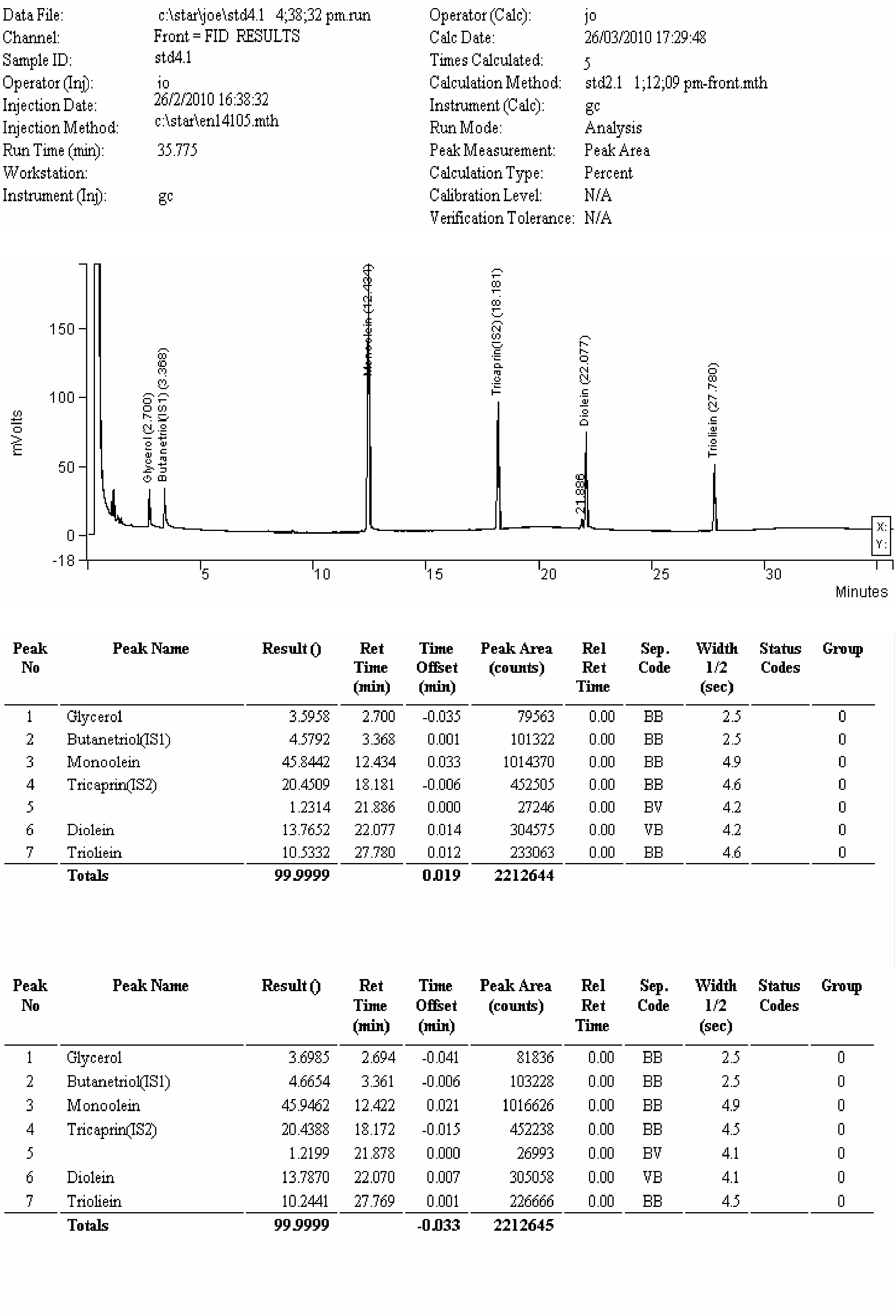
Data File: c:\star\joe\std3.1 2;52;37 pm.run
Channel: Front = FID RESULTS
Sample ID: std3.1
Operator (Inj): io
Injection Date: 26/2/2010 14:52:37
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 26/03/2010 17:28:05
Times Calculated: 3
Calculation Method: std2.1 1;12;09 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Triolein	9.7975	27.772	0.004	172950	0.00	BB	4.4		0
	Totals	**100.0000**		**-0.011**	**1765244**					

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	Triolein	9.5848	27.770	0.002	166770	0.00	BB	4.4		0
	Totals	**100.0000**		**0.002**	**1739943**					

Figure A 3 GC chromatogram of Standard 3



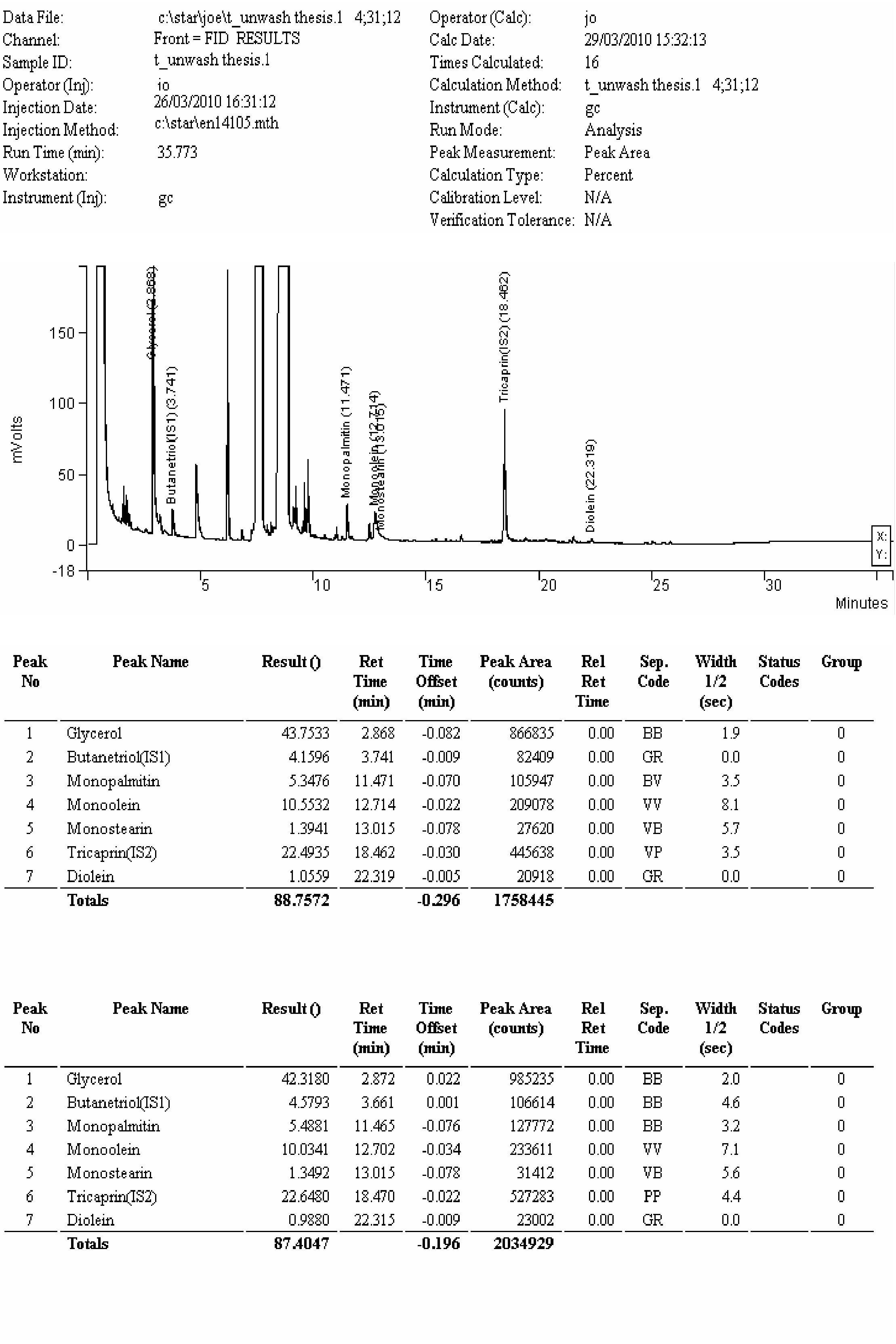
Data File: c:\star\joe\std4.1 4;38;32 pm.run
Channel: Front = FID RESULTS
Sample ID: std4.1
Operator (Inj): jo
Injection Date: 26/2/2010 16:38:32
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 26/03/2010 17:29:48
Times Calculated: 5
Calculation Method: std2.1 1;12;09 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Triolein	10.5332	27.780	0.012	233063	0.00	BB	4.6		0
	Totals	**99.9999**		**0.019**	**2212644**					

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	Triolein	10.2441	27.769	0.001	226666	0.00	BB	4.5		0
	Totals	**99.9999**		**-0.033**	**2212645**					

Figure A 4 GC chromatogram of Standard



Data File: c:\star\joe\t_unwash thesis.1 4;31;12
Channel: Front = FID RESULTS
Sample ID: t_unwash thesis.1
Operator (Inj): io
Injection Date: 26/03/2010 16:31:12
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 29/03/2010 15:32:13
Times Calculated: 16
Calculation Method: t_unwash thesis.1 4;31;12
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

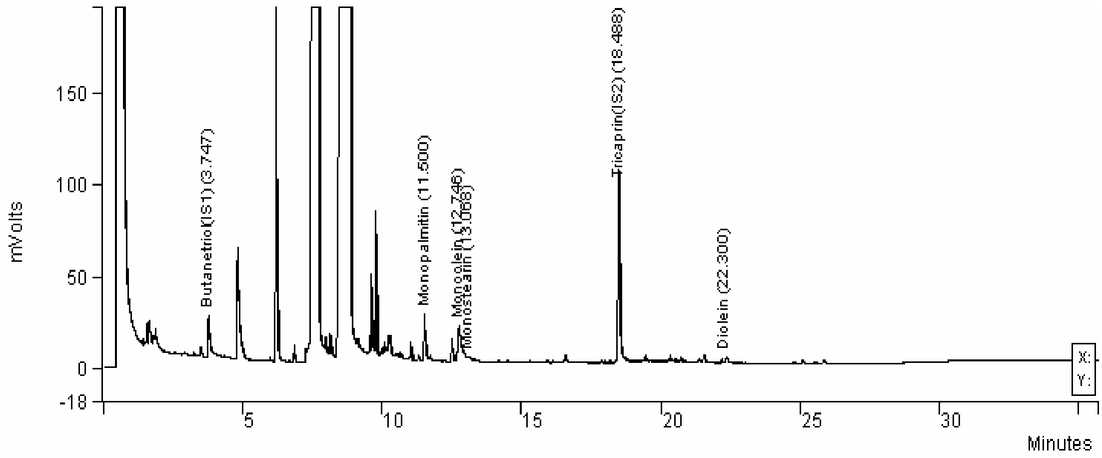
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Glycerol	43.7533	2.868	-0.082	866835	0.00	BB	1.9		0
2	Butanetriol(IS1)	4.1596	3.741	-0.009	82409	0.00	GR	0.0		0
3	Monopalmitin	5.3476	11.471	-0.070	105947	0.00	BV	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	1.0559	22.319	-0.005	20918	0.00	GR	0.0		0
	Totals	**88.7572**		**-0.296**	**1758445**					

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	42.3180	2.872	0.022	985235	0.00	BB	2.0		0
2	Butanetriol(IS1)	4.5793	3.661	0.001	106614	0.00	BB	4.6		0
3	Monopalmitin	5.4881	11.465	-0.076	127772	0.00	BB	3.2		0
4	Monoolein	10.0341	12.702	-0.034	233611	0.00	VV	7.1		0
5	Monostearin	1.3492	13.015	-0.078	31412	0.00	VB	5.6		0
6	Tricaprin(IS2)	22.6480	18.470	-0.022	527283	0.00	PP	4.4		0
7	Diolein	0.9880	22.315	-0.009	23002	0.00	GR	0.0		0
	Totals	**87.4047**		**-0.196**	**2034929**					

Figure A 5 GC chromatogram of free glycerol from crude biodiesel

Data File: c:\star\joe\t_dww thesis.1 6;20;42
Channel: Front = FID RESULTS
Sample ID: t_Dww thesis.1
Operator (Inj): jo
Injection Date: 23/03/2010 18:20:42
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

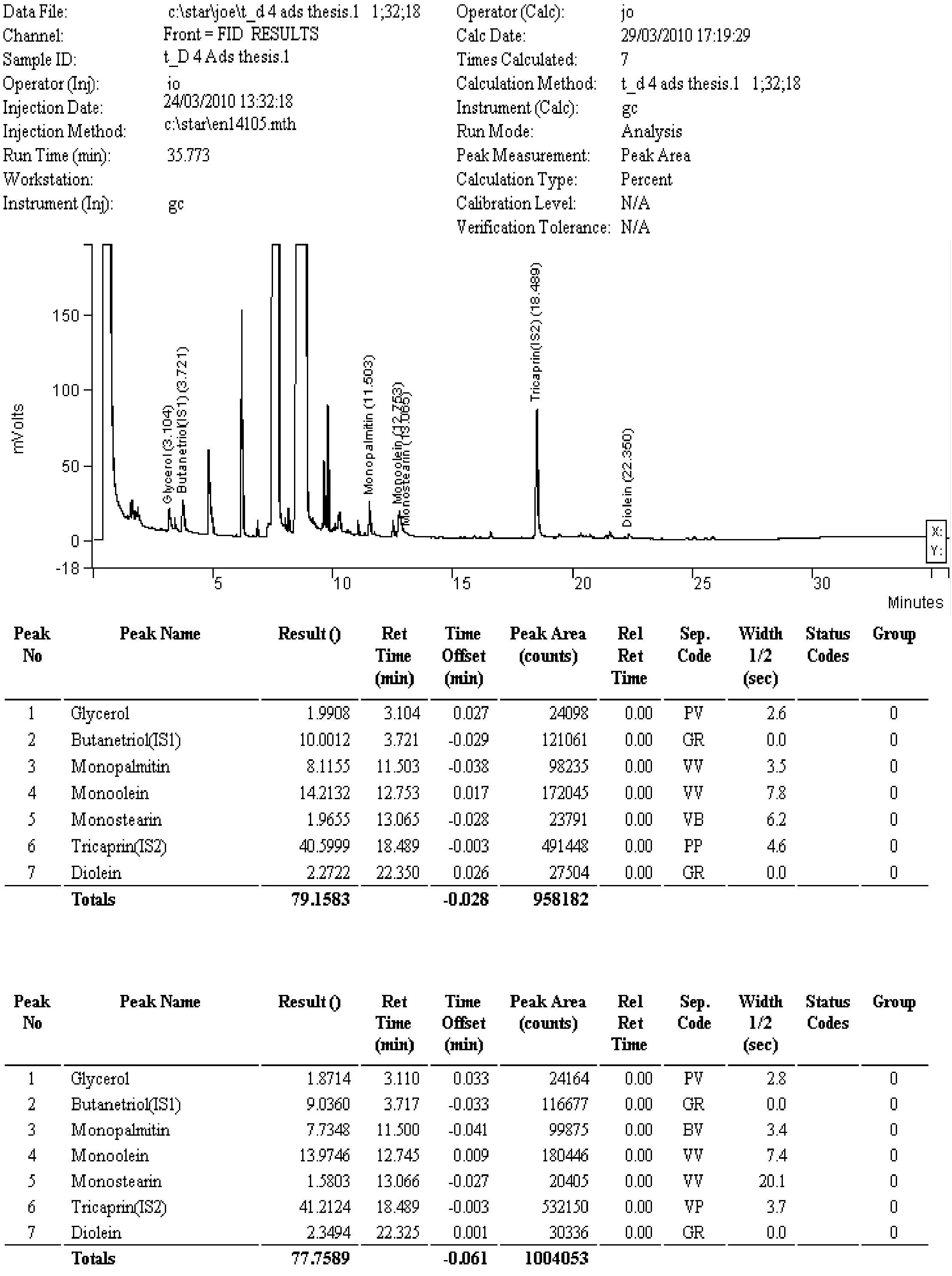
Operator (Calc): jo
Calc Date: 29/03/2010 17:09:30
Times Calculated: 4
Calculation Method: t_dww thesis.1 6;20;42 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



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)	7.3551	3.723	-0.027	83226	0.00	VV	6.2		0
2	Monopalmitin	8.8605	11.495	-0.046	100261	0.00	VV	3.6		0
3	Monoolein	15.4609	12.740	0.004	174947	0.00	VV	7.6		0
4	Monostearin	1.8286	13.044	-0.049	20692	0.00	VV	12.6		0
5	Tricaprin(IS2)	41.2797	18.480	-0.012	467097	0.00	VP	3.6		0
6	Diolein	1.9848	22.275	-0.049	22459	0.00	GR	0.0		0
	Totals	**76.7696**		**-0.179**	**868682**					

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)	9.1235	3.747	-0.003	105730	0.00	VB	5.7		0
2	Monopalmitin	8.4333	11.500	-0.041	97732	0.00	BB	3.5		0
3	Monoolein	16.0513	12.746	0.010	186015	0.00	VV	7.4		0
4	Monostearin	2.2691	13.068	-0.025	26297	0.00	VB	5.5		0
5	Tricaprin(IS2)	43.6348	18.488	-0.004	505675	0.00	VP	3.6		0
6	Diolein	2.4879	22.300	-0.024	28832	0.00	GR	0.0		0
	Totals	**81.9999**		**-0.087**	**950281**					

Figure A 6 GC chromatogram of biodiesel purification by water-washing process



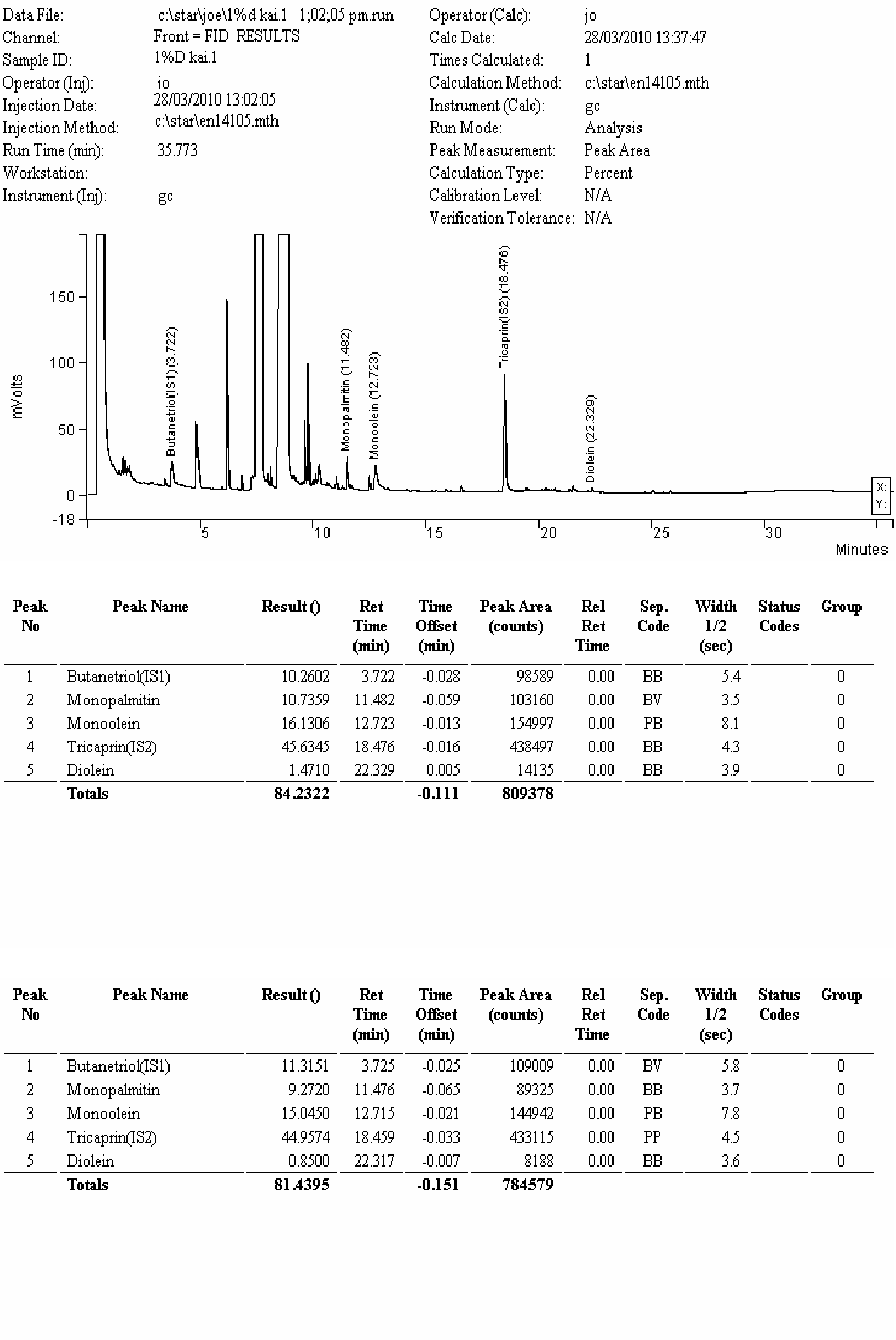
Data File: c:\star\joe\t_d 4 ads thesis.1 1;32;18
Channel: Front = FID RESULTS
Sample ID: t_D 4 Ads thesis.1
Operator (Inj): io
Injection Date: 24/03/2010 13:32:18
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 29/03/2010 17:19:29
Times Calculated: 7
Calculation Method: t_d 4 ads thesis.1 1;32;18
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	1.9908	3.104	0.027	24098	0.00	PV	2.6		0
2	Butanetriol(IS1)	10.0012	3.721	-0.029	121061	0.00	GR	0.0		0
3	Monopalmitin	8.1155	11.503	-0.038	98235	0.00	VV	3.5		0
4	Monoolein	14.2132	12.753	0.017	172045	0.00	VV	7.8		0
5	Monostearin	1.9655	13.065	-0.028	23791	0.00	VB	6.2		0
6	Tricaprin(IS2)	40.5999	18.489	-0.003	491448	0.00	PP	4.6		0
7	Diolein	2.2722	22.350	0.026	27504	0.00	GR	0.0		0
	Totals	**79.1583**		**-0.028**	**958182**					

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	1.8714	3.110	0.033	24164	0.00	PV	2.8		0
2	Butanetriol(IS1)	9.0360	3.717	-0.033	116677	0.00	GR	0.0		0
3	Monopalmitin	7.7348	11.500	-0.041	99875	0.00	BV	3.4		0
4	Monoolein	13.9746	12.745	0.009	180446	0.00	VV	7.4		0
5	Monostearin	1.5803	13.066	-0.027	20405	0.00	VV	20.1		0
6	Tricaprin(IS2)	41.2124	18.489	-0.003	532150	0.00	VP	3.7		0
7	Diolein	2.3494	22.325	0.001	30336	0.00	GR	0.0		0
	Totals	**77.7589**		**-0.061**	**1004053**					

Figure A7 GC chromatogram of biodiesel purification by dry water-washing process with 4% natural diatomite



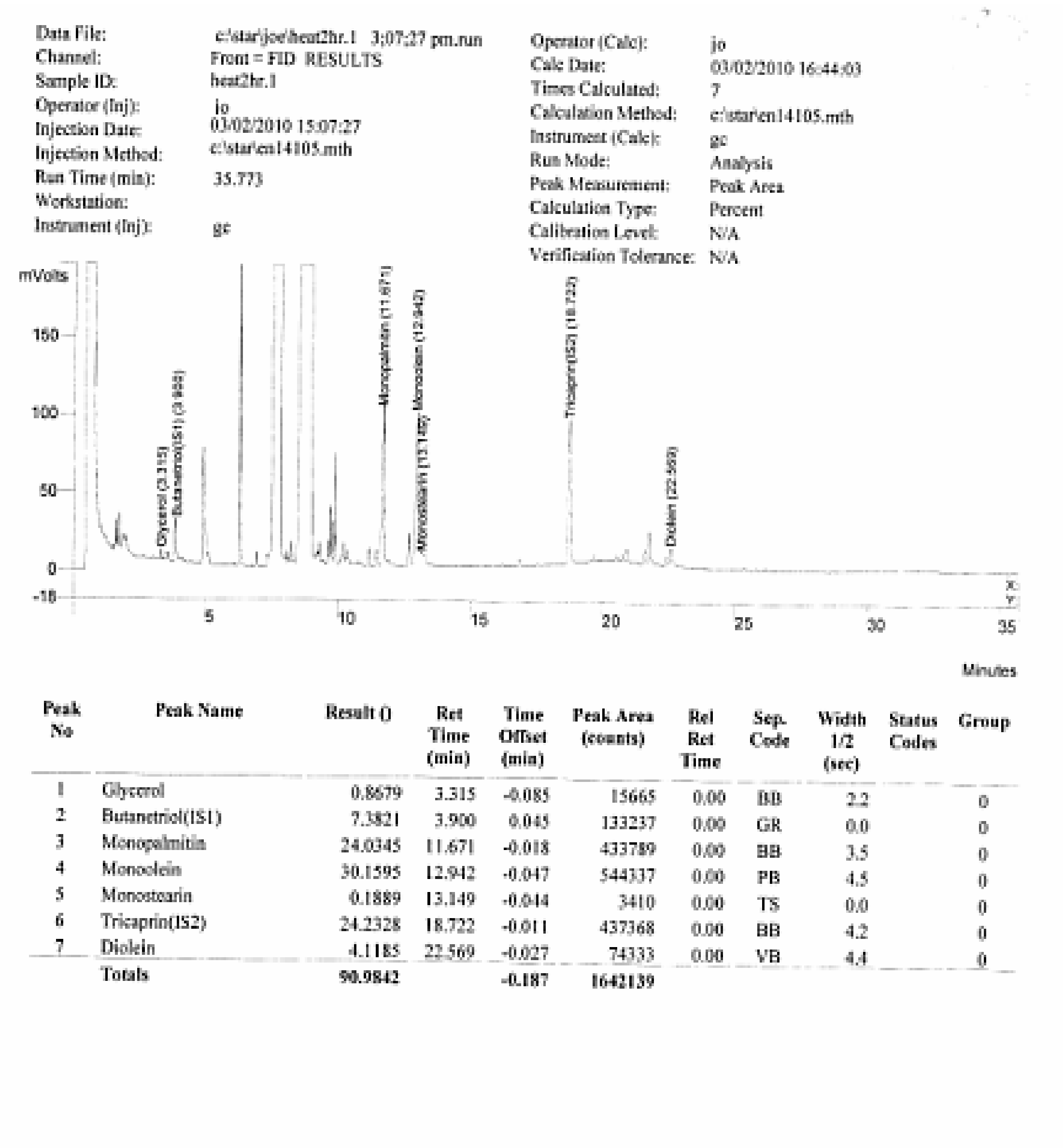
Data File: c:\star\joe\1%d kai.1 1;02;05 pm.run
Channel: Front = FID RESULTS
Sample ID: 1%D kai.1
Operator (Inj): jo
Injection Date: 28/03/2010 13:02:05
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 28/03/2010 13:37:47
Times Calculated: 1
Calculation Method: c:\star\en14105.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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)	10.2602	3.722	-0.028	98589	0.00	BB	5.4		0
2	Monopalmitin	10.7359	11.482	-0.059	103160	0.00	BV	3.5		0
3	Monoolein	16.1306	12.723	-0.013	154997	0.00	PB	8.1		0
4	Tricaprin(IS2)	45.6345	18.476	-0.016	438497	0.00	BB	4.3		0
5	Diolein	1.4710	22.329	0.005	14135	0.00	BB	3.9		0
	Totals	**84.2322**		**-0.111**	**809378**					

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)	11.3151	3.725	-0.025	109009	0.00	BV	5.8		0
2	Monopalmitin	9.2720	11.476	-0.065	89325	0.00	BB	3.7		0
3	Monoolein	15.0450	12.715	-0.021	144942	0.00	PB	7.8		0
4	Tricaprin(IS2)	44.9574	18.459	-0.033	433115	0.00	PP	4.5		0
5	Diolein	0.8500	22.317	-0.007	8188	0.00	BB	3.6		0
	Totals	**81.4395**		**-0.151**	**784579**					

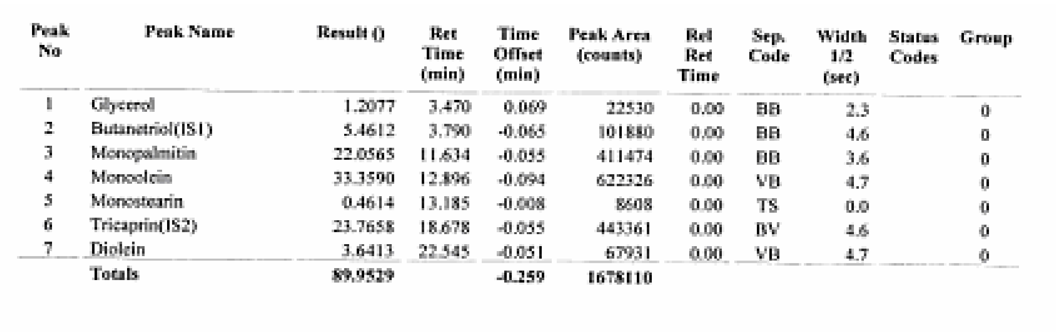
Figure A 8 GC chromatogram of biodiesel purification by dry water-washing process with 1%D via methanol removals



Data File: c:\star\joe\heat2hr.1 3;07;27 pm.run
Channel: Front = FID RESULTS
Sample ID: heat2hr.1
Operator (Inj): jo
Injection Date: 03/02/2010 15:07:27
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

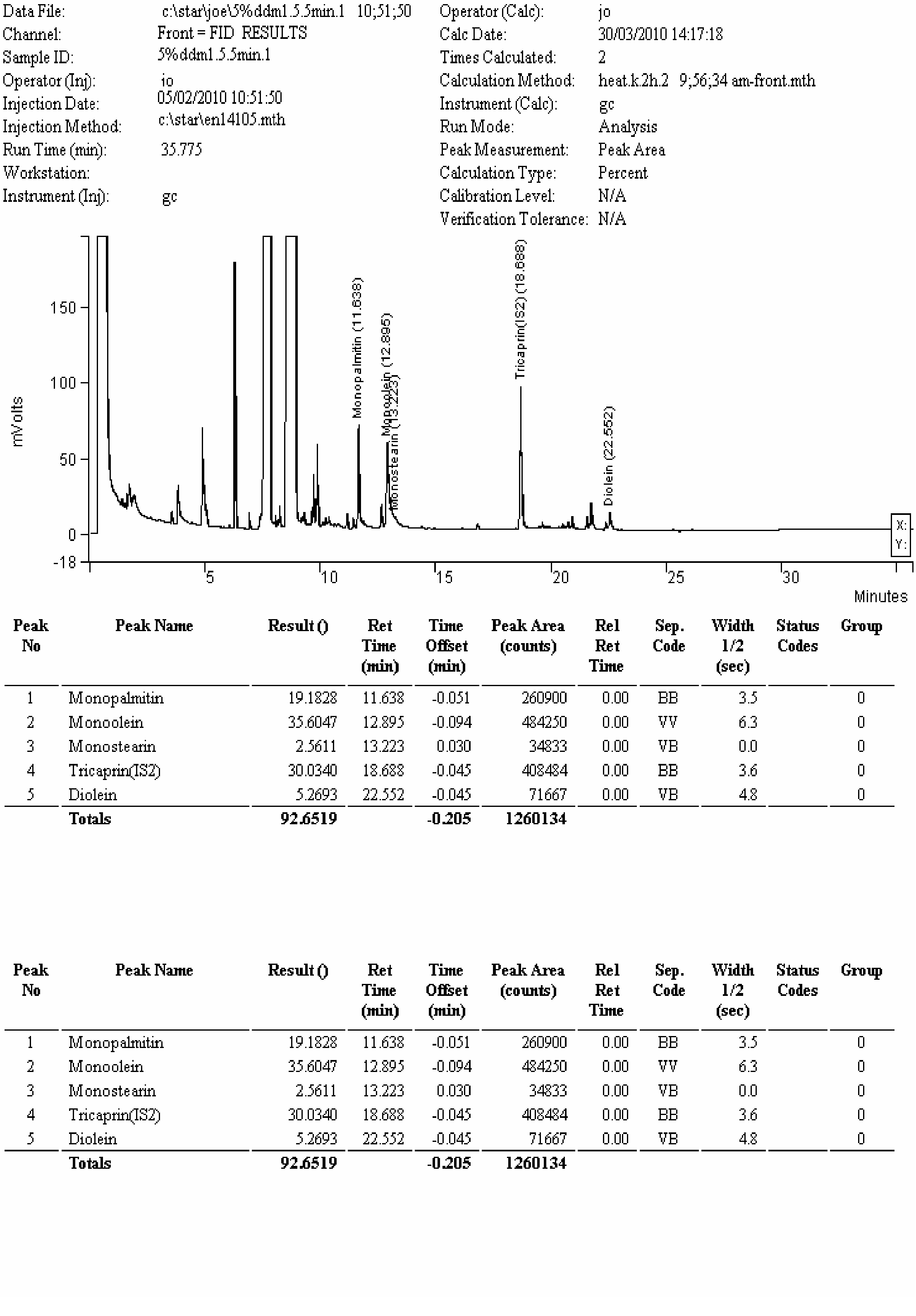
Operator (Calc): jo
Calc Date: 03/02/2010 16:44:03
Times Calculated: 7
Calculation Method: c:\star\en14105.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

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	0.8679	3.315	-0.085	15665	0.00	BB	2.2		0
2	Butanetriol(IS1)	7.3821	3.900	0.045	133237	0.00	GR	0.0		0
3	Monopalmitin	24.0345	11.671	-0.018	433789	0.00	BB	3.5		0
4	Monoolein	30.1595	12.942	-0.047	544337	0.00	PB	4.5		0
5	Monostearin	0.1889	13.149	-0.044	3410	0.00	TS	0.0		0
6	Tricaprin(IS2)	24.2328	18.722	-0.011	437368	0.00	BB	4.2		0
7	Diolein	4.1185	22.569	-0.027	74333	0.00	VB	4.4		0
	Totals	90.9842		-0.187	1642139					



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	1.2077	3.470	0.069	22530	0.00	BB	2.3		0
2	Butanetriol(IS1)	5.4612	3.790	-0.065	101880	0.00	BB	4.6		0
3	Monopalmitin	22.0565	11.634	-0.055	411474	0.00	BB	3.6		0
4	Monoolein	33.3590	12.896	-0.094	622326	0.00	VB	4.7		0
5	Monostearin	0.4614	13.185	-0.008	8608	0.00	TS	0.0		0
6	Tricaprin(IS2)	23.7658	18.678	-0.055	443361	0.00	BV	4.6		0
7	Diolein	3.6413	22.545	-0.051	67931	0.00	VB	4.7		0
	Totals	89.9529		-0.259	1678110					

Figure A 9 GC chromatogram of High % monoglyceride content in Biodiesel 5



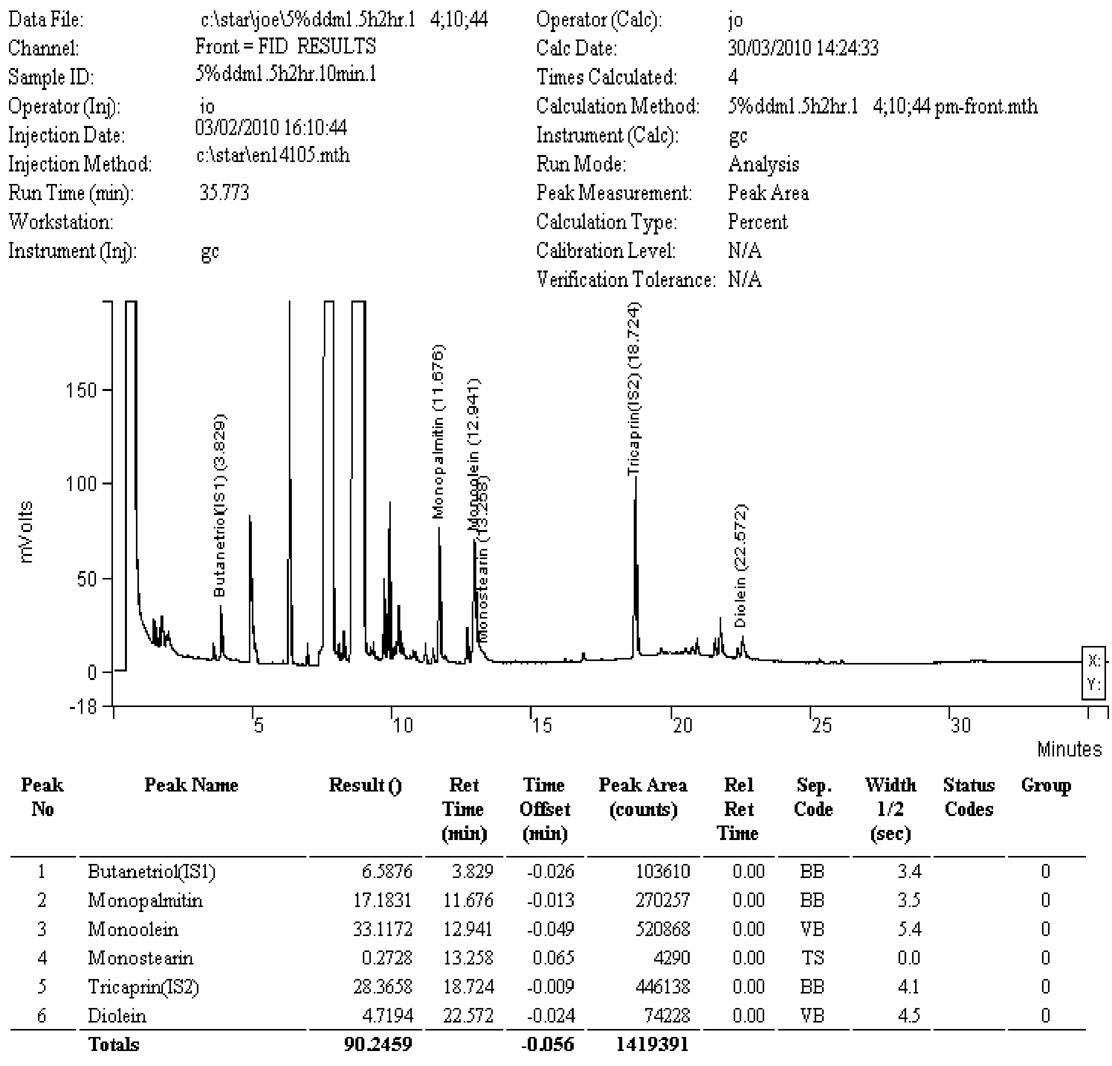
Data File: c:\star\joe\5%ddm1.5.5min.1 10;51;50
Channel: Front = FID RESULTS
Sample ID: 5%ddm1.5.5min.1
Operator (Inj): jo
Injection Date: 05/02/2010 10:51:50
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 14:17:18
Times Calculated: 2
Calculation Method: heat.k2h.2 9;56;34 am-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	19.1828	11.638	-0.051	260900	0.00	BB	3.5		0
2	Monoolein	35.6047	12.895	-0.094	484250	0.00	VV	6.3		0
3	Monostearin	2.5611	13.223	0.030	34833	0.00	VB	0.0		0
4	Tricaprin(IS2)	30.0340	18.688	-0.045	408484	0.00	BB	3.6		0
5	Diolein	5.2693	22.552	-0.045	71667	0.00	VB	4.8		0
	Totals	**92.6519**		**-0.205**	**1260134**					

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	Monopalmitin	19.1828	11.638	-0.051	260900	0.00	BB	3.5		0
2	Monoolein	35.6047	12.895	-0.094	484250	0.00	VV	6.3		0
3	Monostearin	2.5611	13.223	0.030	34833	0.00	VB	0.0		0
4	Tricaprin(IS2)	30.0340	18.688	-0.045	408484	0.00	BB	3.6		0
5	Diolein	5.2693	22.552	-0.045	71667	0.00	VB	4.8		0
	Totals	**92.6519**		**-0.205**	**1260134**					

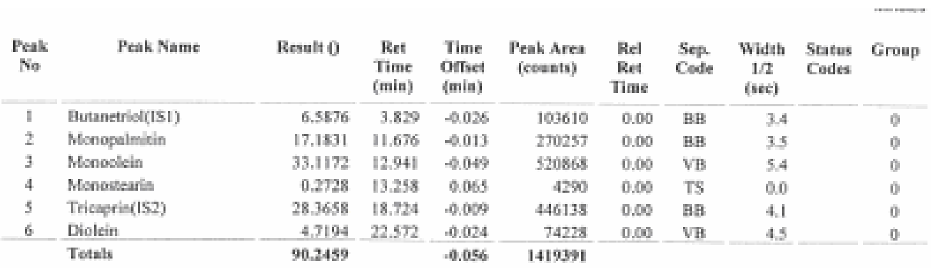
Figure A 10 GC chromatogram of effect of contact time on monoglyceride removal with 5%DDM1.5 (5minute)
5/10min



Data File: c:\star\joe\5%ddm1.5h2hr.1 4;10;44
Channel: Front = FID RESULTS
Sample ID: 5%ddm1.5h2hr.10min.1
Operator (Inj): jo
Injection Date: 03/02/2010 16:10:44
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

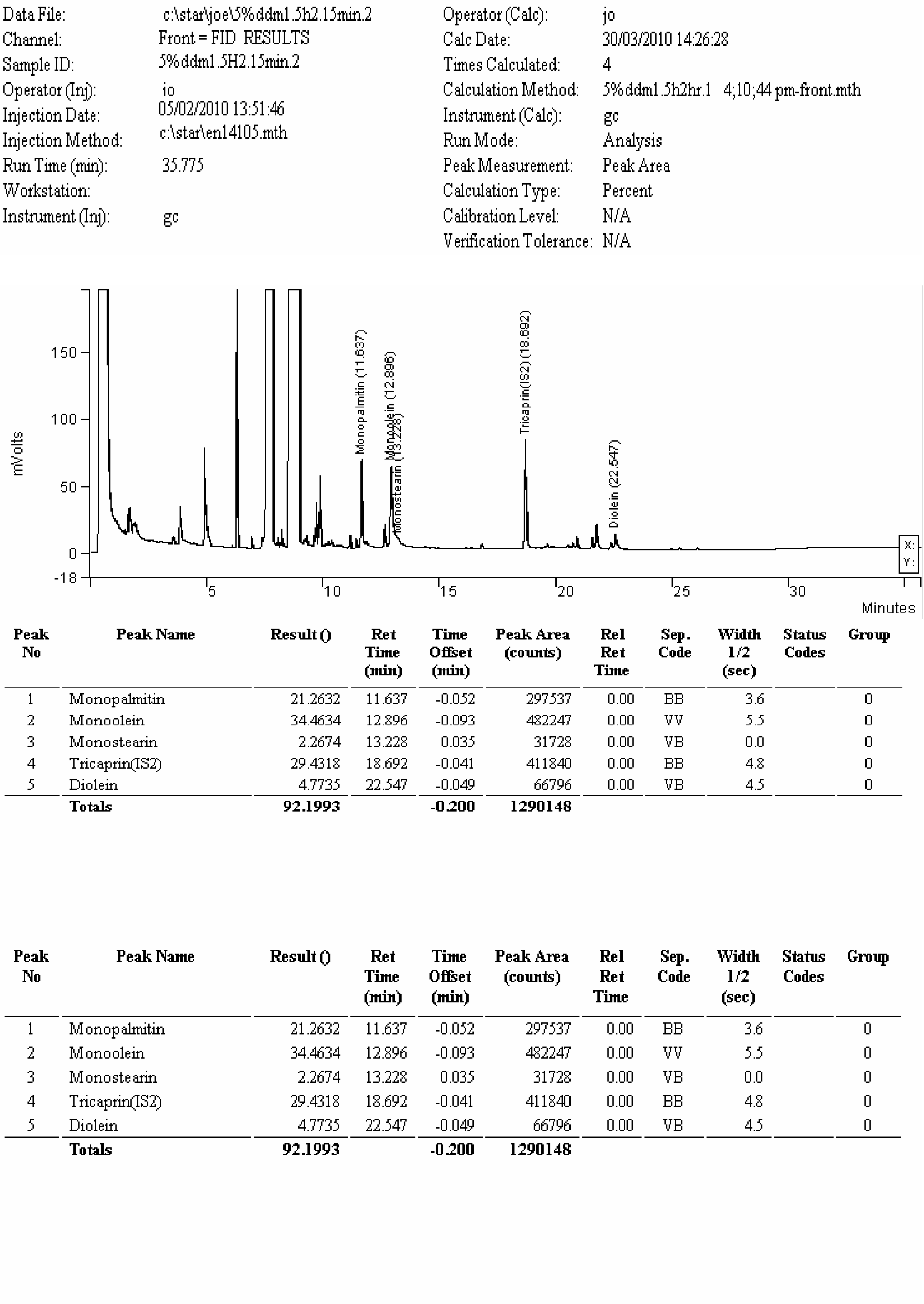
Operator (Calc): jo
Calc Date: 30/03/2010 14:24:33
Times Calculated: 4
Calculation Method: 5%ddm1.5h2hr.1 4;10;44 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

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)	6.5876	3.829	-0.026	103610	0.00	BB	3.4		0
2	Monopalmitin	17.1831	11.676	-0.013	270257	0.00	BB	3.5		0
3	Monoolein	33.1172	12.941	-0.049	520868	0.00	VB	5.4		0
4	Monostearin	0.2728	13.258	0.065	4290	0.00	TS	0.0		0
5	Tricaprin(IS2)	28.3658	18.724	-0.009	446138	0.00	BB	4.1		0
6	Diolein	4.7194	22.572	-0.024	74228	0.00	VB	4.5		0
	Totals	**90.2459**		**-0.056**	**1419391**					



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)	6.5876	3.829	-0.026	103610	0.00	BB	3.4		0
2	Monopalmitin	17.1831	11.676	-0.013	270257	0.00	BB	3.5		0
3	Monoolein	33.1172	12.941	-0.049	520868	0.00	VB	5.4		0
4	Monostearin	0.2728	13.258	0.065	4290	0.00	TS	0.0		0
5	Tricaprin(IS2)	28.3658	18.724	-0.009	446138	0.00	BB	4.1		0
6	Diolein	4.7194	22.572	-0.024	74228	0.00	VB	4.5		0
	Totals	**90.2459**		**-0.056**	**1419391**					

Figure A 11 GC chromatogram of effect of contact time on monoglyceride removal with 5%DDM1.5 (10minute)



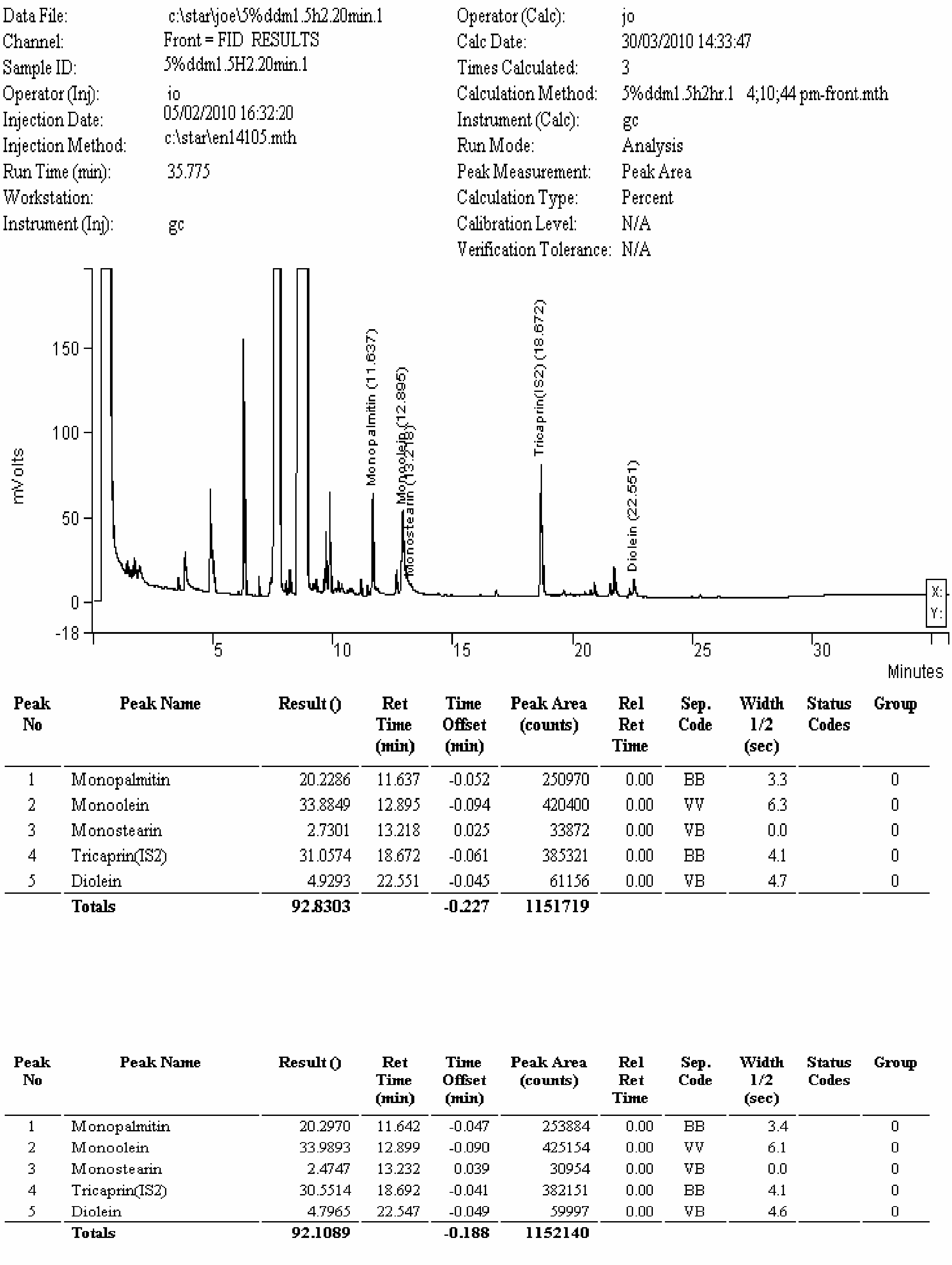
Data File: c:\star\joe\5%ddml.5h2.15min.2
Channel: Front = FID RESULTS
Sample ID: 5%ddml.5H2.15min.2
Operator (Inj): io
Injection Date: 05/02/2010 13:51:46
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 14:26:28
Times Calculated: 4
Calculation Method: 5%ddml.5h2hr.1 4;10;44 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	21.2632	11.637	-0.052	297537	0.00	BB	3.6		0
2	Monoolein	34.4634	12.896	-0.093	482247	0.00	VV	5.5		0
3	Monostearin	2.2674	13.228	0.035	31728	0.00	VB	0.0		0
4	Tricaprin(IS2)	29.4318	18.692	-0.041	411840	0.00	BB	4.8		0
5	Diolein	4.7735	22.547	-0.049	66796	0.00	VB	4.5		0
	Totals	**92.1993**		**-0.200**	**1290148**					

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	Monopalmitin	21.2632	11.637	-0.052	297537	0.00	BB	3.6		0
2	Monoolein	34.4634	12.896	-0.093	482247	0.00	VV	5.5		0
3	Monostearin	2.2674	13.228	0.035	31728	0.00	VB	0.0		0
4	Tricaprin(IS2)	29.4318	18.692	-0.041	411840	0.00	BB	4.8		0
5	Diolein	4.7735	22.547	-0.049	66796	0.00	VB	4.5		0
	Totals	**92.1993**		**-0.200**	**1290148**					

Figure A12 GC chromatogram of effect of contact time on monoglyceride removal with 5%DDM1.5 (15minute)



Data File: c:\star\joe\5%ddm1.5h2.20min.1
Channel: Front = FID RESULTS
Sample ID: 5%ddm1.5H2.20min.1
Operator (Inj): io
Injection Date: 05/02/2010 16:32:20
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 14:33:47
Times Calculated: 3
Calculation Method: 5%ddm1.5h2hr.1 4;10;44 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

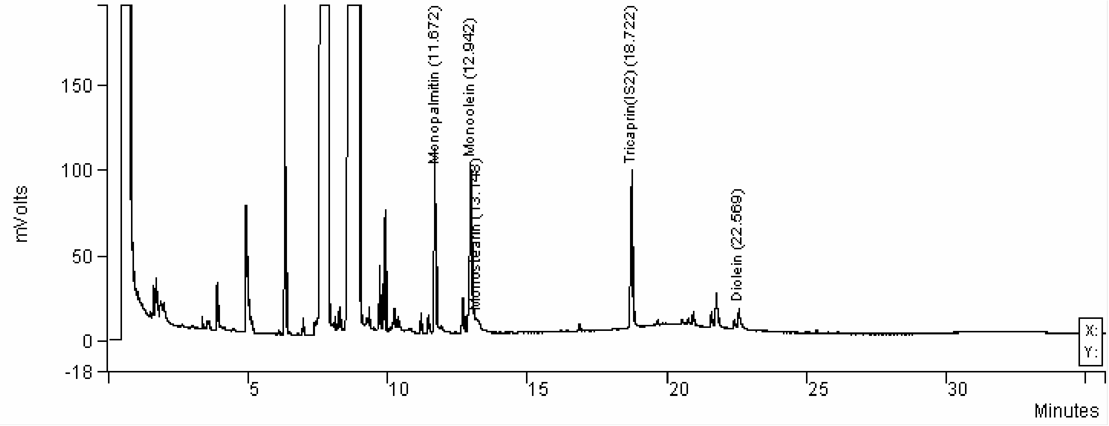
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Monopalmitin	20.2286	11.637	-0.052	250970	0.00	BB	3.3		0
2	Monoolein	33.8849	12.895	-0.094	420400	0.00	VV	6.3		0
3	Monostearin	2.7301	13.218	0.025	33872	0.00	VB	0.0		0
4	Tricaprin(IS2)	31.0574	18.672	-0.061	385321	0.00	BB	4.1		0
5	Diolein	4.9293	22.551	-0.045	61156	0.00	VB	4.7		0
	Totals	**92.8303**		**-0.227**	**1151719**					

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	Monopalmitin	20.2970	11.642	-0.047	253884	0.00	BB	3.4		0
2	Monoolein	33.9893	12.899	-0.090	425154	0.00	VV	6.1		0
3	Monostearin	2.4747	13.232	0.039	30954	0.00	VB	0.0		0
4	Tricaprin(IS2)	30.5514	18.692	-0.041	382151	0.00	BB	4.1		0
5	Diolein	4.7965	22.547	-0.049	59997	0.00	VB	4.6		0
	Totals	**92.1089**		**-0.188**	**1152140**					

Figure A 13 GC chromatogram of effect of contact time on monoglyceride removal with 5%DDM1.5 (20minute)

Data File: c:\star\joe\heat2hr.1 3;07;27 pm.run
Channel: Front = FID RESULTS
Sample ID: heat2hr.1
Operator (Inj): io
Injection Date: 03/02/2010 15:07:27
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 14:08:21
Times Calculated: 13
Calculation Method: heat.k.2h.2 9;56;34 am-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



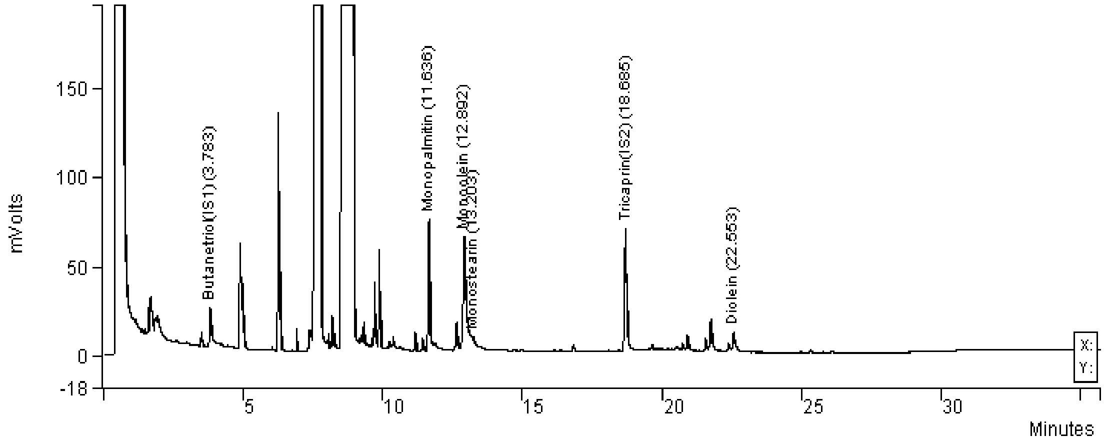
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Monopalmitin	25.2263	11.672	-0.017	402802	0.00	BB	3.5		0
2	Monoolein	34.0528	12.942	-0.047	543740	0.00	PB	4.5		0
3	Monostearin	0.2133	13.148	-0.045	3406	0.00	TS	0.0		0
4	Tricaprin(IS2)	27.2884	18.722	-0.011	435729	0.00	BB	4.2		0
5	Diolein	4.6672	22.569	-0.027	74523	0.00	VB	4.4		0
	Totals	**91.4480**		**-0.147**	**1460200**					

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	Monopalmitin	25.2263	11.672	-0.017	402802	0.00	BB	3.5		0
2	Monoolein	34.0528	12.942	-0.047	543740	0.00	PB	4.5		0
3	Monostearin	0.2133	13.148	-0.045	3406	0.00	TS	0.0		0
4	Tricaprin(IS2)	27.2884	18.722	-0.011	435729	0.00	BB	4.2		0
5	Diolein	4.6672	22.569	-0.027	74523	0.00	VB	4.4		0
	Totals	**91.4480**		**-0.147**	**1460200**					

Figure A 14 GC chromatogram of high % monoglyceride content in biodiesel
ดูประสิทธิภาพของตัวดูดซับ_mono

Data File: c:\star\joe\k.5%dh2.2 11;57;24 am.run
Channel: Front = FID RESULTS
Sample ID: k.5%dh2.2
Operator (Inj): io
Injection Date: 04/02/2010 11:57:24
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

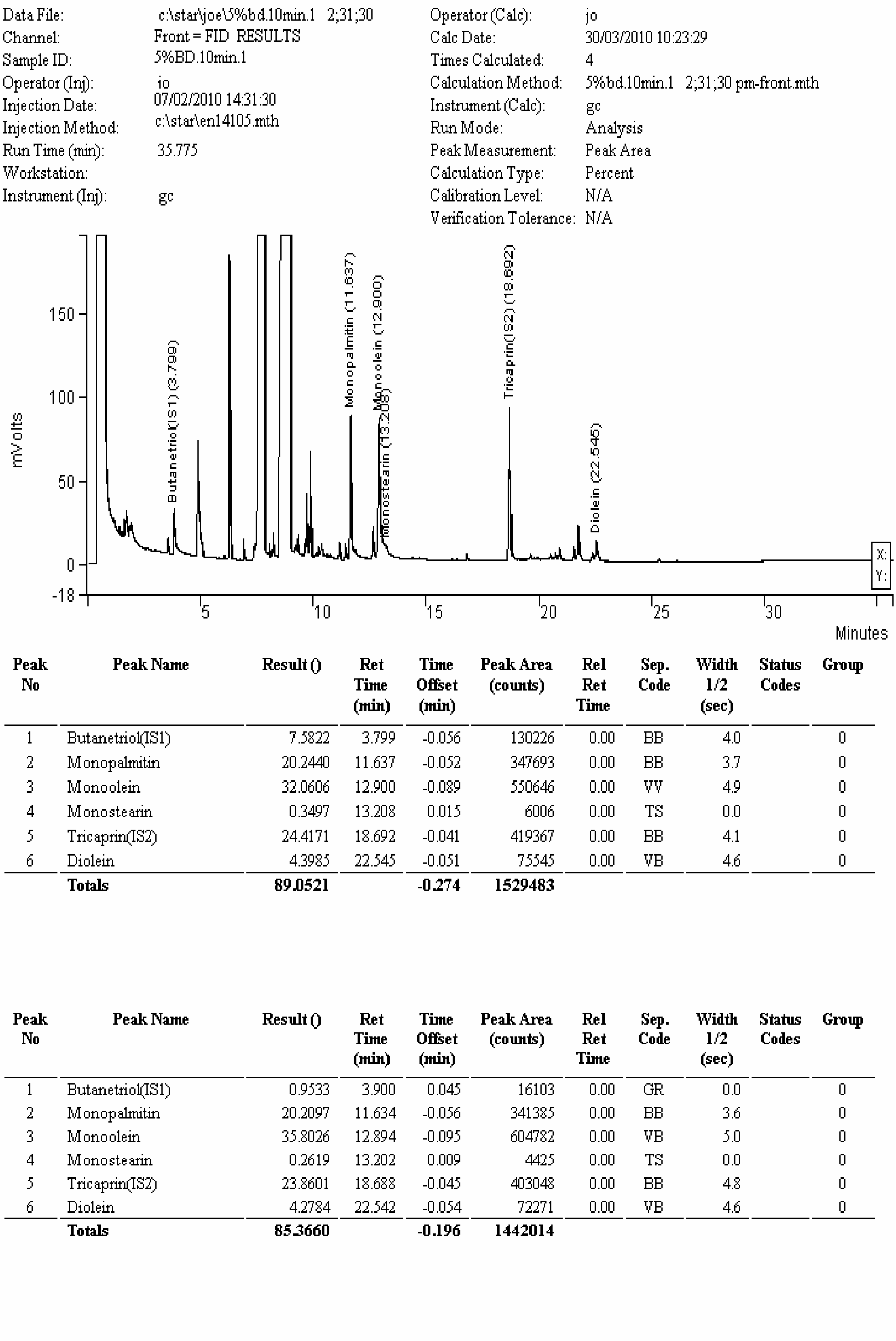
Operator (Calc): jo
Calc Date: 30/03/2010 14:12:04
Times Calculated: 4
Calculation Method: heat.k2h.2 9;56;34 am-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



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)	0.6807	3.783	-0.072	9294	0.00	BB	0.0		0
2	Monopalmitin	20.3469	11.636	-0.053	277796	0.00	BB	3.5		0
3	Monoolein	36.6745	12.892	-0.097	500716	0.00	VV	5.5		0
4	Monostearin	3.1207	13.203	0.010	42606	0.00	VB	0.0		0
5	Tricaprin(IS2)	27.9433	18.685	-0.048	381509	0.00	BB	5.0		0
6	Diolein	4.4069	22.553	-0.043	60167	0.00	VB	4.8		0
	Totals	**93.1730**		**-0.303**	**1272088**					

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	Monopalmitin	22.8740	11.644	-0.045	333433	0.00	BB	3.5		0
2	Monoolein	33.6293	12.905	-0.084	490213	0.00	VV	5.3		0
3	Monostearin	2.4326	13.225	0.032	35460	0.00	VB	0.0		0
4	Tricaprin(IS2)	27.2031	18.697	-0.036	396539	0.00	BB	4.6		0
5	Diolein	4.1499	22.558	-0.038	60493	0.00	VB	4.4		0
	Totals	**90.2889**		**-0.171**	**1316138**					

Figure A 15 GC chromatogram of monoglyceride removal with 5%Natural diatomite



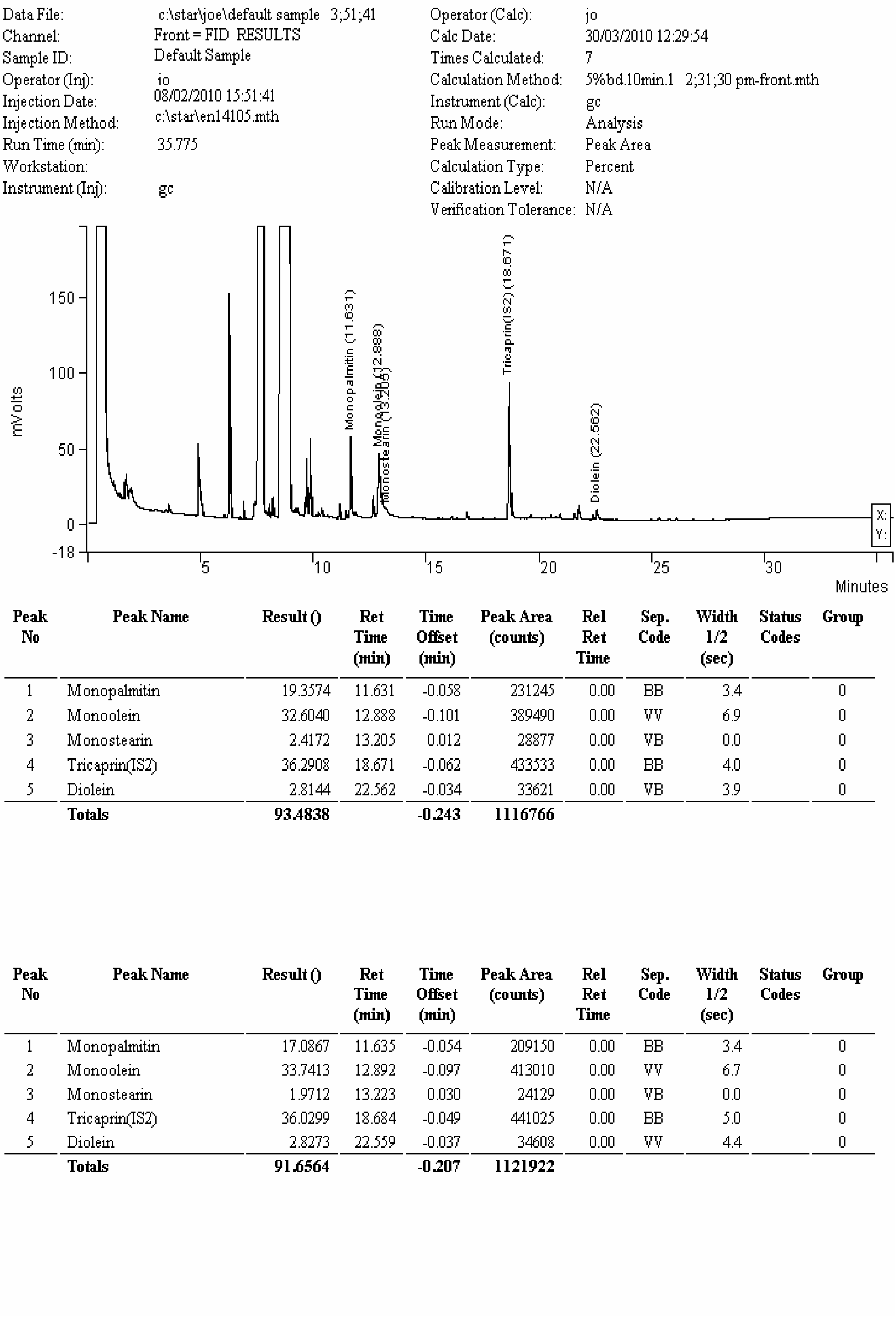
Data File: c:\star\joe\5%bd.10min.1 2;31;30
Channel: Front = FID RESULTS
Sample ID: 5%BD.10min.1
Operator (Inj): io
Injection Date: 07/02/2010 14:31:30
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 10:23:29
Times Calculated: 4
Calculation Method: 5%bd.10min.1 2;31;30 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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)	7.5822	3.799	-0.056	130226	0.00	BB	4.0		0
2	Monopalmitin	20.2440	11.637	-0.052	347693	0.00	BB	3.7		0
3	Monoolein	32.0606	12.900	-0.089	550646	0.00	VV	4.9		0
4	Monostearin	0.3497	13.208	0.015	6006	0.00	TS	0.0		0
5	Tricaprin(IS2)	24.4171	18.692	-0.041	419367	0.00	BB	4.1		0
6	Diolein	4.3985	22.545	-0.051	75545	0.00	VB	4.6		0
	Totals	**89.0521**		**-0.274**	**1529483**					

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)	0.9533	3.900	0.045	16103	0.00	GR	0.0		0
2	Monopalmitin	20.2097	11.634	-0.056	341385	0.00	BB	3.6		0
3	Monoolein	35.8026	12.894	-0.095	604782	0.00	VB	5.0		0
4	Monostearin	0.2619	13.202	0.009	4425	0.00	TS	0.0		0
5	Tricaprin(IS2)	23.8601	18.688	-0.045	403048	0.00	BB	4.8		0
6	Diolein	4.2784	22.542	-0.054	72271	0.00	VB	4.6		0
	Totals	**85.3660**		**-0.196**	**1442014**					

Figure A 16 GC chromatogram of monoglyceride removal with 5% burn natural diatomite



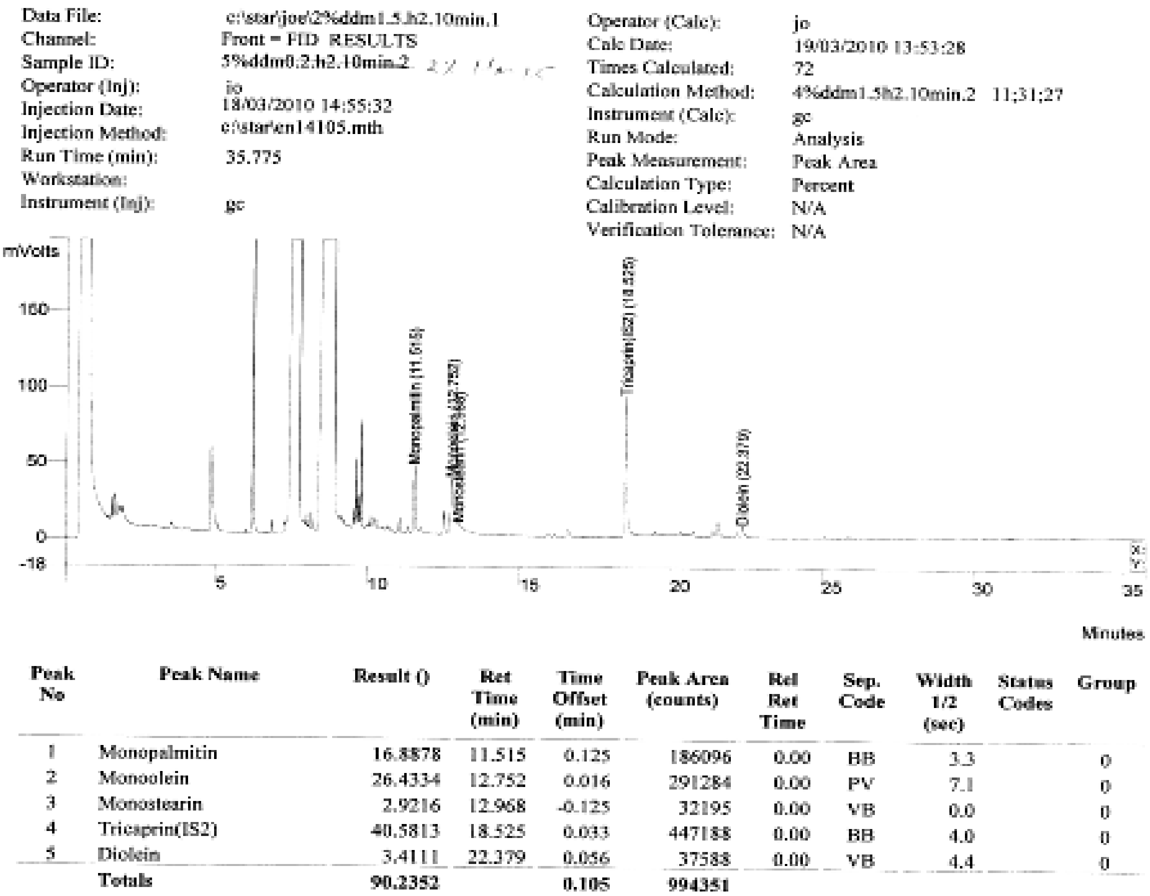
Data File: c:\star\joe\default sample 3;51;41
Channel: Front = FID RESULTS
Sample ID: Default Sample
Operator (Inj): jo
Injection Date: 08/02/2010 15:51:41
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 12:29:54
Times Calculated: 7
Calculation Method: 5%bd.10min.1 2;31;30 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	19.3574	11.631	-0.058	231245	0.00	BB	3.4		0
2	Monoolein	32.6040	12.888	-0.101	389490	0.00	VV	6.9		0
3	Monostearin	2.4172	13.205	0.012	28877	0.00	VB	0.0		0
4	Tricaprin(IS2)	36.2908	18.671	-0.062	433533	0.00	BB	4.0		0
5	Diolein	2.8144	22.562	-0.034	33621	0.00	VB	3.9		0
	Totals	**93.4838**		**-0.243**	**1116766**					

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	Monopalmitin	17.0867	11.635	-0.054	209150	0.00	BB	3.4		0
2	Monoolein	33.7413	12.892	-0.097	413010	0.00	VV	6.7		0
3	Monostearin	1.9712	13.223	0.030	24129	0.00	VB	0.0		0
4	Tricaprin(IS2)	36.0299	18.684	-0.049	441025	0.00	BB	5.0		0
5	Diolein	2.8273	22.559	-0.037	34608	0.00	VV	4.4		0
	Totals	**91.6564**		**-0.207**	**1121922**					

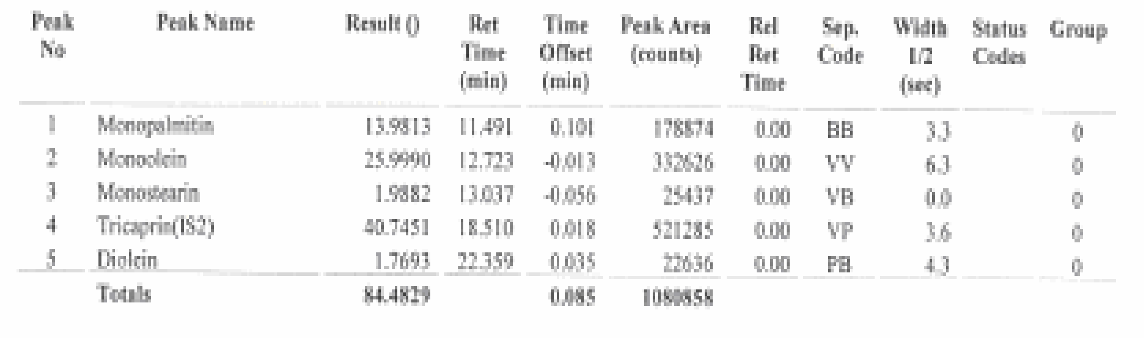
Figure A17 GC chromatogram high % monoglyceride



Data File: c:\star\joe\2%ddm1.5.h2.10min.1
Channel: Front = FID RESULTS
Sample ID: 5%ddm0.2.h2.10min.2 [illegible]
Operator (Inj): jo
Injection Date: 18/03/2010 14:55:32
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

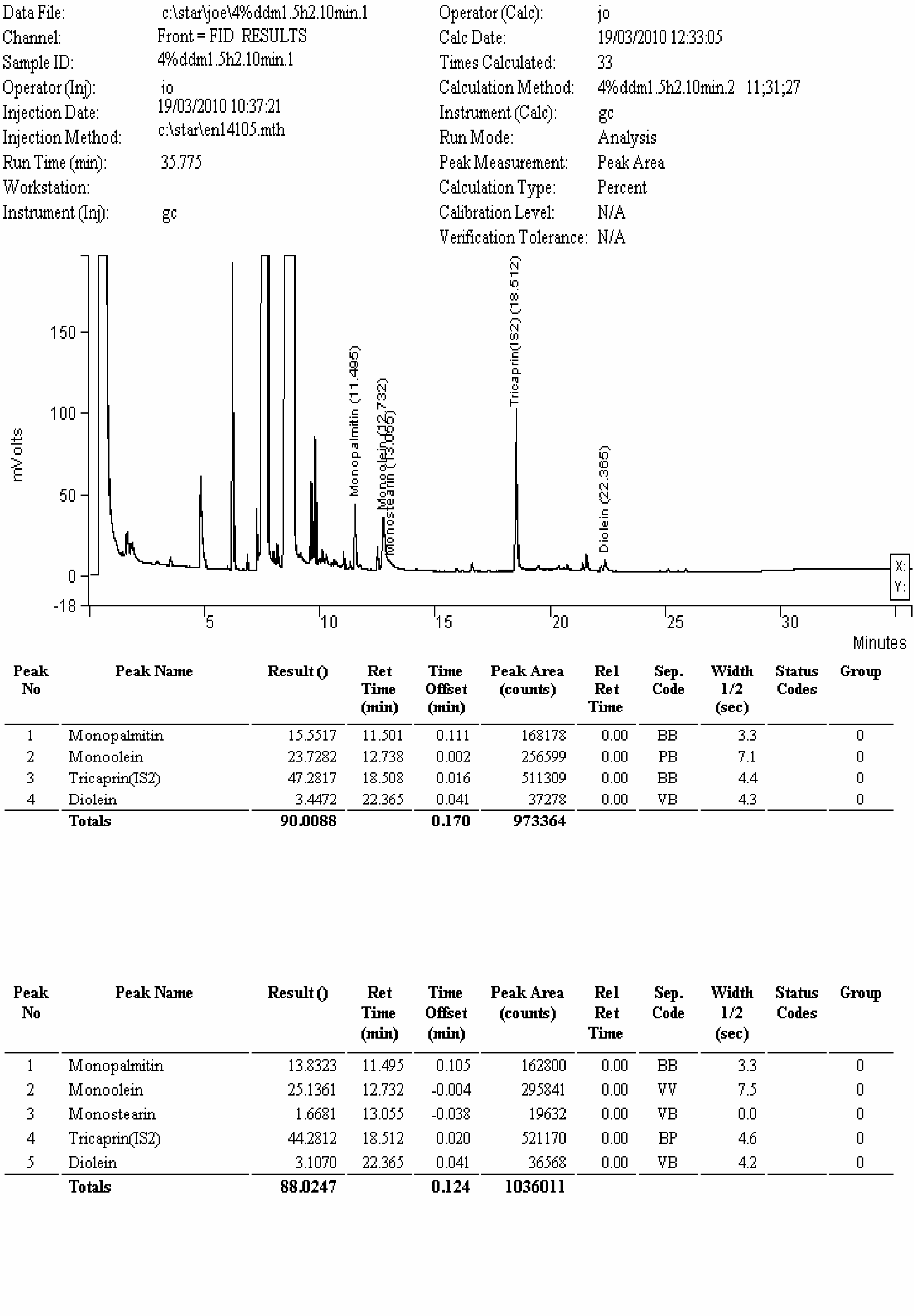
Operator (Calc): jo
Calc Date: 19/03/2010 13:53:28
Times Calculated: 72
Calculation Method: 4%ddm1.5h2.10min.2 11;31;27
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

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	Monopalmitin	16.8878	11.515	0.125	186096	0.00	BB	3.3		0
2	Monoolein	26.4334	12.752	0.016	291284	0.00	PV	7.1		0
3	Monostearin	2.9216	12.968	-0.125	32195	0.00	VB	0.0		0
4	Tricaprin(IS2)	40.5813	18.525	0.033	447188	0.00	BB	4.0		0
5	Diolein	3.4111	22.379	0.056	37588	0.00	VB	4.4		0
	Totals	**90.2352**		**0.105**	**994351**					



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	Monopalmitin	13.9813	11.491	0.101	178874	0.00	BB	3.3		0
2	Monoolein	25.9990	12.723	-0.013	332626	0.00	VV	6.3		0
3	Monostearin	1.9882	13.037	-0.056	25437	0.00	VB	0.0		0
4	Tricaprin(IS2)	40.7451	18.510	0.018	521285	0.00	VP	3.6		0
5	Diolein	1.7693	22.359	0.035	22636	0.00	PB	4.3		0
	Totals	**84.4829**		**0.085**	**1080858**					

Figure A18 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (2%DDM1.5)



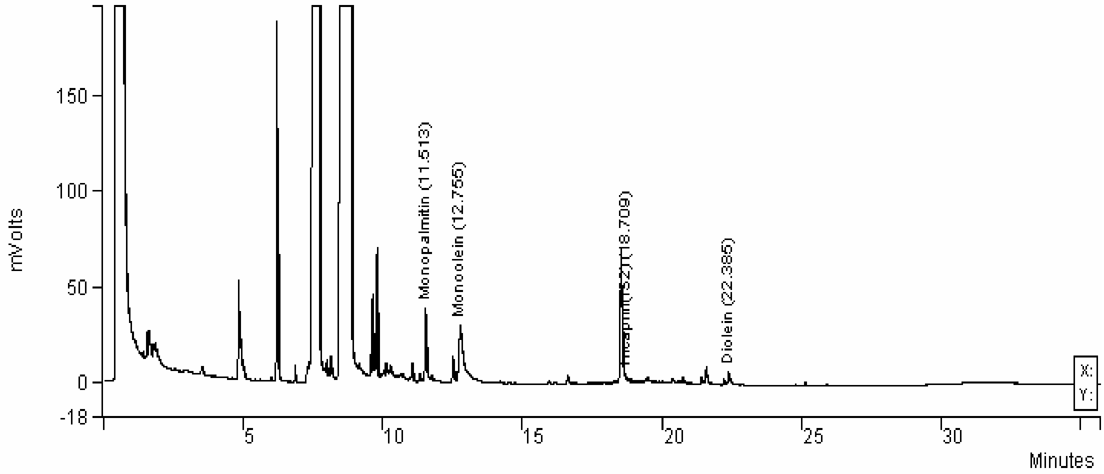
Data File:	c:\star\joe\4%ddm1.5h2.10min.1	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	19/03/2010 12:33:05
Sample ID:	4%ddm1.5h2.10min.1	Times Calculated:	33
Operator (Inj):	io	Calculation Method:	4%ddm1.5h2.10min.2 11;31;27
Injection Date:	19/03/2010 10:37:21	Instrument (Calc):	gc
Injection 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	Monopalmitin	15.5517	11.501	0.111	168178	0.00	BB	3.3		0
2	Monoolein	23.7282	12.738	0.002	256599	0.00	PB	7.1		0
3	Tricaprin(IS2)	47.2817	18.508	0.016	511309	0.00	BB	4.4		0
4	Diolein	3.4472	22.365	0.041	37278	0.00	VB	4.3		0
	Totals	**90.0088**		**0.170**	**973364**					

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	Monopalmitin	13.8323	11.495	0.105	162800	0.00	BB	3.3		0
2	Monoolein	25.1361	12.732	-0.004	295841	0.00	VV	7.5		0
3	Monostearin	1.6681	13.055	-0.038	19632	0.00	VB	0.0		0
4	Tricaprin(IS2)	44.2812	18.512	0.020	521170	0.00	BP	4.6		0
5	Diolein	3.1070	22.365	0.041	36568	0.00	VB	4.2		0
	Totals	**88.0247**		**0.124**	**1036011**					

Figure A19 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (4%DDM1.5)

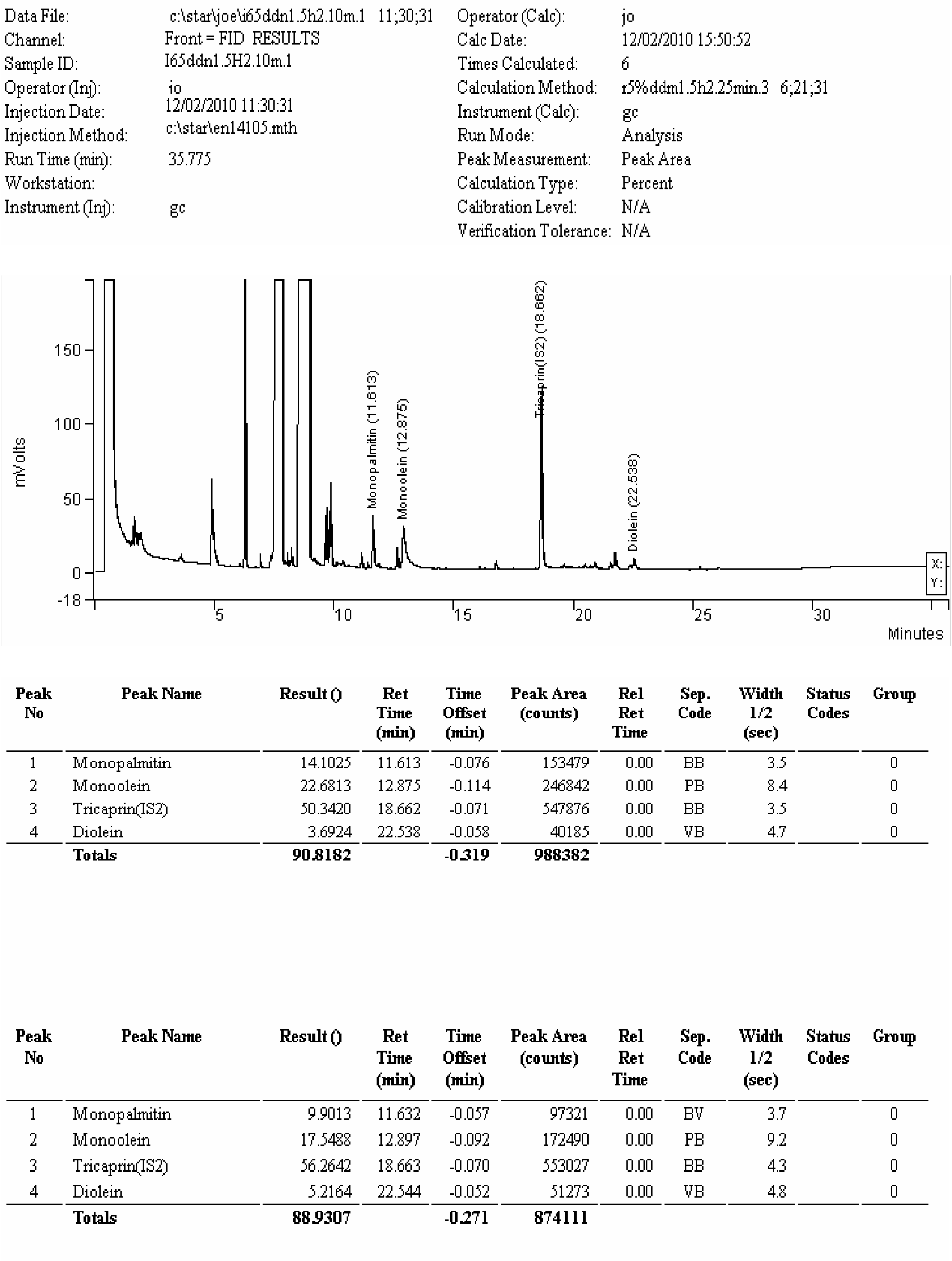
Data File:	c:\star\joe\5%ddm1.5h2.10m.1	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	30/03/2010 10:23:29
Sample ID:	5%ddm1.5H2.10m.1	Times Calculated:	74
Operator (Inj):	io	Calculation Method:	5%bd.10min.1 2;31;30 pm-front.mth
Injection Date:	18/03/2010 11:17:37	Instrument (Calc):	gc
Injection 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	Monopalmitin	4.3965	11.513	-0.176	18482	0.00	BB	1.0		0
2	Monoolein	57.5230	12.755	-0.234	241817	0.00	BB	7.7		0
3	Tricaprin(IS2)	0.4970	18.709	-0.024	2089	0.00	BP	0.9		0
4	Diolein	4.1480	22.385	-0.211	17438	0.00	BB	4.0		0
	Totals	**66.5645**		**-0.645**	**279826**					

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	Monopalmitin	16.0473	11.647	-0.042	159049	0.00	BB	3.5		0
2	Monoolein	28.1291	12.908	-0.081	278796	0.00	PB	7.5		0
3	Tricaprin(IS2)	44.8766	18.697	-0.036	444785	0.00	BB	4.9		0
4	Diolein	3.6660	22.579	-0.017	36334	0.00	VB	4.6		0
	Totals	**92.7190**		**-0.176**	**918964**					

Figure A20 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (5%DDM1.5)



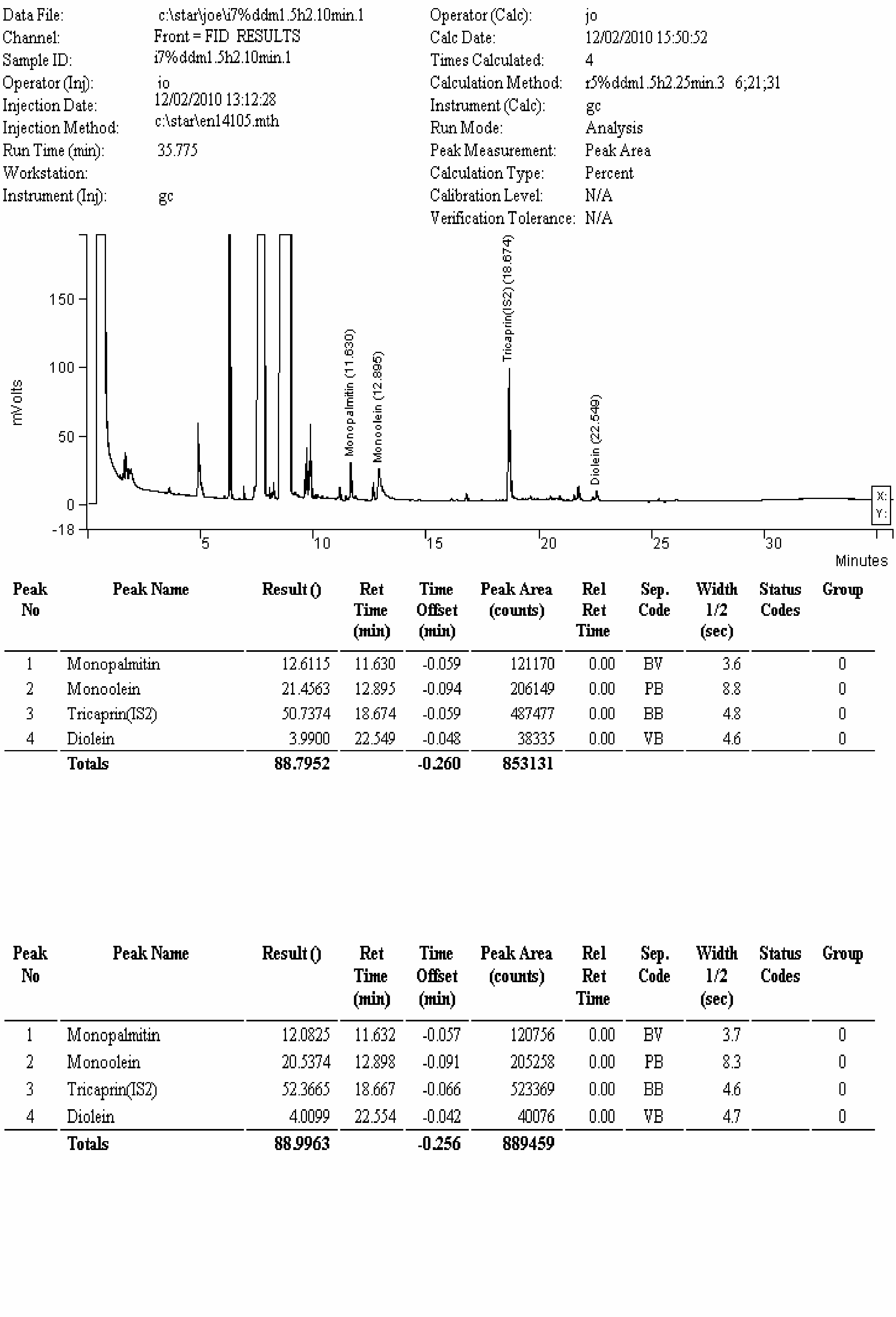
Data File: c:\star\joe\i65ddn1.5h2.10m.1 11;30;31
Channel: Front = FID RESULTS
Sample ID: I65ddn1.5H2.10m.1
Operator (Inj): io
Injection Date: 12/02/2010 11:30:31
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 12/02/2010 15:50:52
Times Calculated: 6
Calculation Method: r5%ddm1.5h2.25min.3 6;21;31
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	14.1025	11.613	-0.076	153479	0.00	BB	3.5		0
2	Monoolein	22.6813	12.875	-0.114	246842	0.00	PB	8.4		0
3	Tricaprin(IS2)	50.3420	18.662	-0.071	547876	0.00	BB	3.5		0
4	Diolein	3.6924	22.538	-0.058	40185	0.00	VB	4.7		0
	Totals	**90.8182**		**-0.319**	**988382**					

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	Monopalmitin	9.9013	11.632	-0.057	97321	0.00	BV	3.7		0
2	Monoolein	17.5488	12.897	-0.092	172490	0.00	PB	9.2		0
3	Tricaprin(IS2)	56.2642	18.663	-0.070	553027	0.00	BB	4.3		0
4	Diolein	5.2164	22.544	-0.052	51273	0.00	VB	4.8		0
	Totals	**88.9307**		**-0.271**	**874111**					

Figure A21 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (6%DDM1.5)



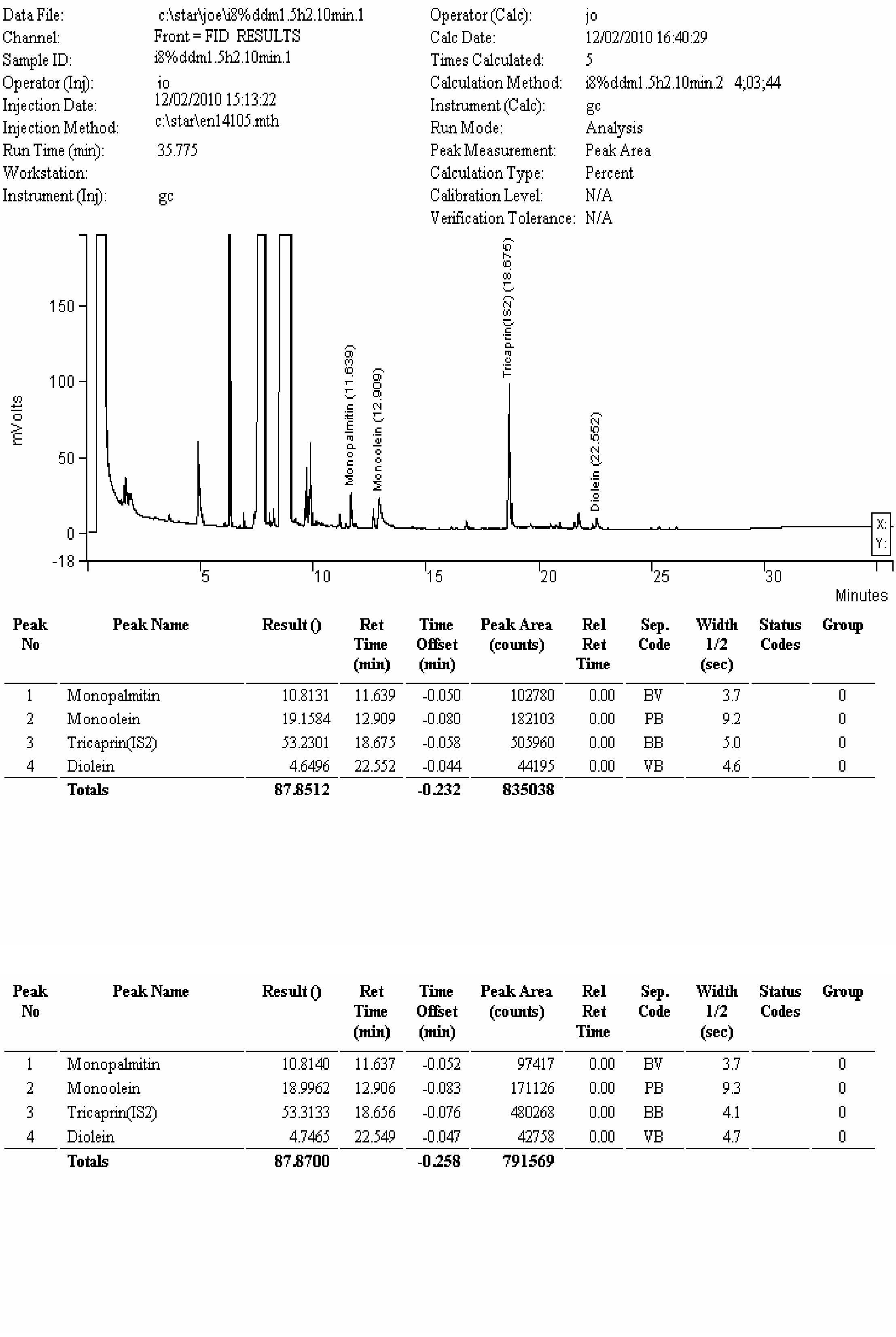
Data File: c:\star\joe\i7%ddm1.5h2.10min.1
Channel: Front = FID RESULTS
Sample ID: i7%ddm1.5h2.10min.1
Operator (Inj): io
Injection Date: 12/02/2010 13:12:28
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 12/02/2010 15:50:52
Times Calculated: 4
Calculation Method: r5%ddm1.5h2.25min.3 6;21;31
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	12.6115	11.630	-0.059	121170	0.00	BV	3.6		0
2	Monoolein	21.4563	12.895	-0.094	206149	0.00	PB	8.8		0
3	Tricaprin(IS2)	50.7374	18.674	-0.059	487477	0.00	BB	4.8		0
4	Diolein	3.9900	22.549	-0.048	38335	0.00	VB	4.6		0
	Totals	**88.7952**		**-0.260**	**853131**					

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	Monopalmitin	12.0825	11.632	-0.057	120756	0.00	BV	3.7		0
2	Monoolein	20.5374	12.898	-0.091	205258	0.00	PB	8.3		0
3	Tricaprin(IS2)	52.3665	18.667	-0.066	523369	0.00	BB	4.6		0
4	Diolein	4.0099	22.554	-0.042	40076	0.00	VB	4.7		0
	Totals	**88.9963**		**-0.256**	**889459**					

Figure A22 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (7%DDM1.5)



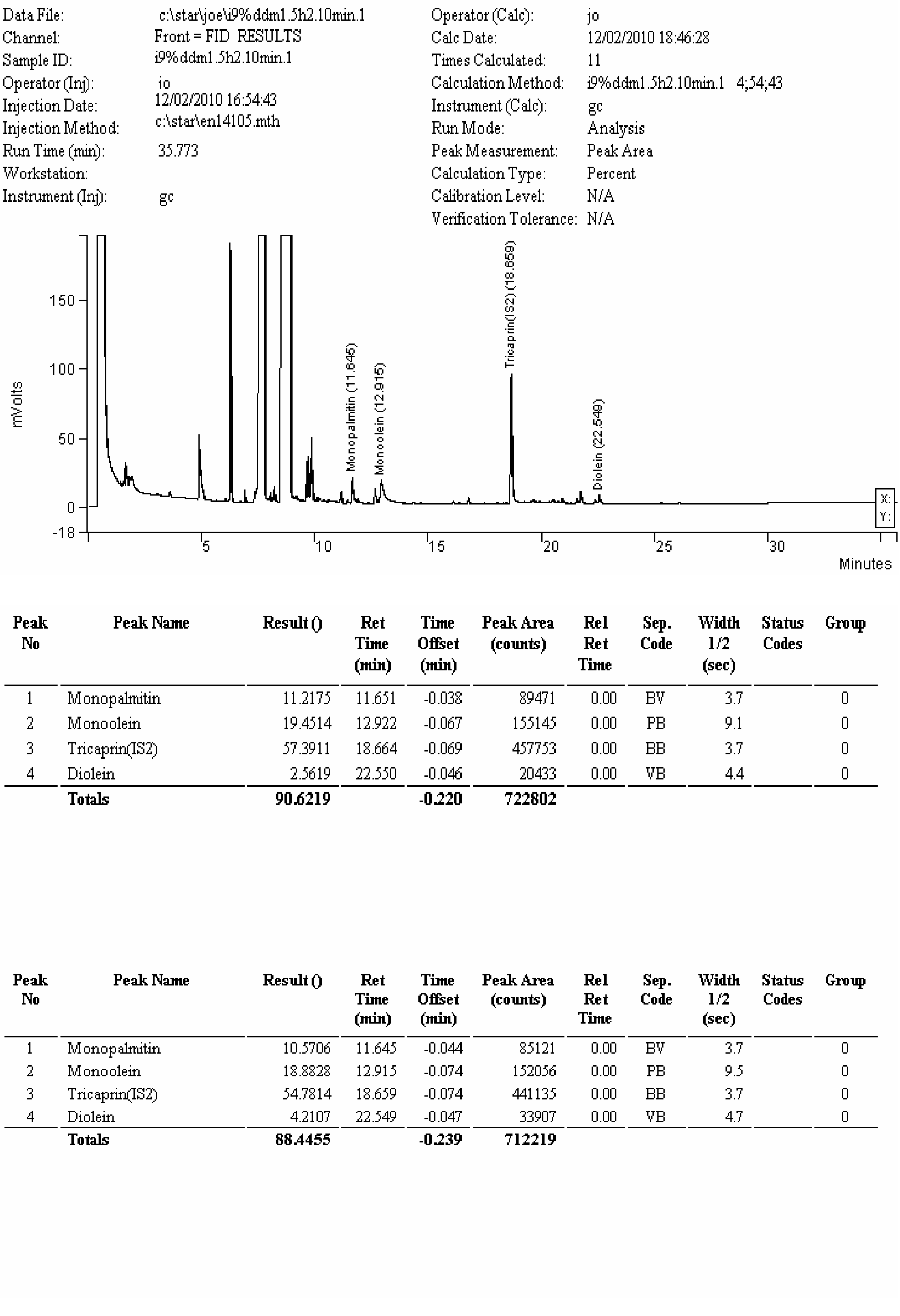
Data File: c:\star\joe\i8%ddm1.5h2.10min.1
Channel: Front = FID RESULTS
Sample ID: i8%ddm1.5h2.10min.1
Operator (Inj): io
Injection Date: 12/02/2010 15:13:22
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 12/02/2010 16:40:29
Times Calculated: 5
Calculation Method: i8%ddm1.5h2.10min.2 4;03;44
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	10.8131	11.639	-0.050	102780	0.00	BV	3.7		0
2	Monoolein	19.1584	12.909	-0.080	182103	0.00	PB	9.2		0
3	Tricaprin(IS2)	53.2301	18.675	-0.058	505960	0.00	BB	5.0		0
4	Diolein	4.6496	22.552	-0.044	44195	0.00	VB	4.6		0
	Totals	**87.8512**		**-0.232**	**835038**					

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	Monopalmitin	10.8140	11.637	-0.052	97417	0.00	BV	3.7		0
2	Monoolein	18.9962	12.906	-0.083	171126	0.00	PB	9.3		0
3	Tricaprin(IS2)	53.3133	18.656	-0.076	480268	0.00	BB	4.1		0
4	Diolein	4.7465	22.549	-0.047	42758	0.00	VB	4.7		0
	Totals	**87.8700**		**-0.258**	**791569**					

Figure A23 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (8%DDM1.5)

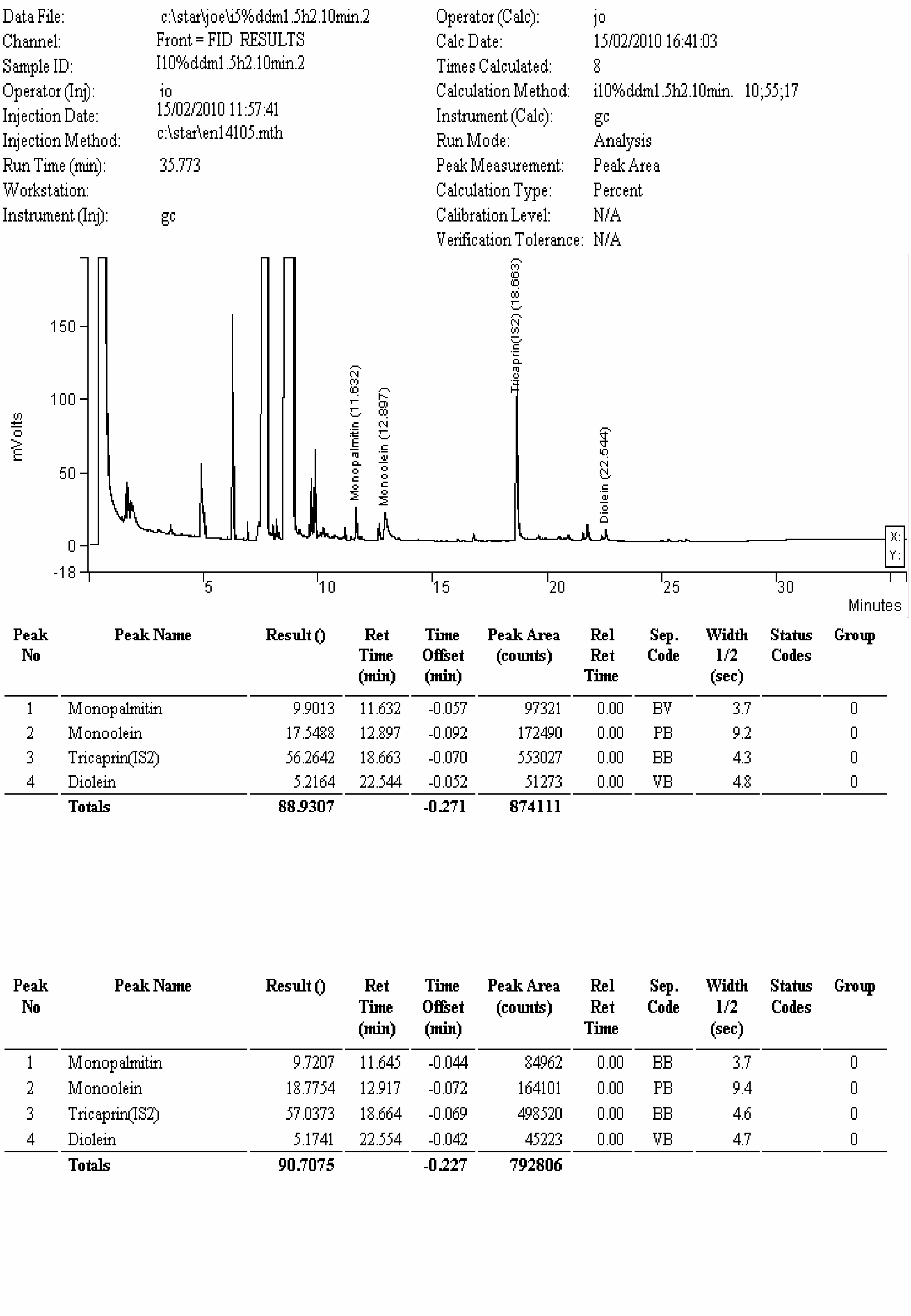


Data File:	c:\star\joe\i9%ddm1.5h2.10min.1	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	12/02/2010 18:46:28
Sample ID:	i9%ddm1.5h2.10min.1	Times Calculated:	11
Operator (Inj):	io	Calculation Method:	i9%ddm1.5h2.10min.1 4;54;43
Injection Date:	12/02/2010 16:54:43	Instrument (Calc):	gc
Injection 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	Monopalmitin	11.2175	11.651	-0.038	89471	0.00	BV	3.7		0
2	Monoolein	19.4514	12.922	-0.067	155145	0.00	PB	9.1		0
3	Tricaprin(IS2)	57.3911	18.664	-0.069	457753	0.00	BB	3.7		0
4	Diolein	2.5619	22.550	-0.046	20433	0.00	VB	4.4		0
	Totals	**90.6219**		**-0.220**	**722802**					

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	Monopalmitin	10.5706	11.645	-0.044	85121	0.00	BV	3.7		0
2	Monoolein	18.8828	12.915	-0.074	152056	0.00	PB	9.5		0
3	Tricaprin(IS2)	54.7814	18.659	-0.074	441135	0.00	BB	3.7		0
4	Diolein	4.2107	22.549	-0.047	33907	0.00	VB	4.7		0
	Totals	**88.4455**		**-0.239**	**712219**					

Figure A24 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (9%DDM1.5)



Data File: c:\star\joe\i5%ddm1.5h2.10min.2
Channel: Front = FID RESULTS
Sample ID: I10%ddm1.5h2.10min.2
Operator (Inj): io
Injection Date: 15/02/2010 11:57:41
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 15/02/2010 16:41:03
Times Calculated: 8
Calculation Method: i10%ddm1.5h2.10min. 10;55;17
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

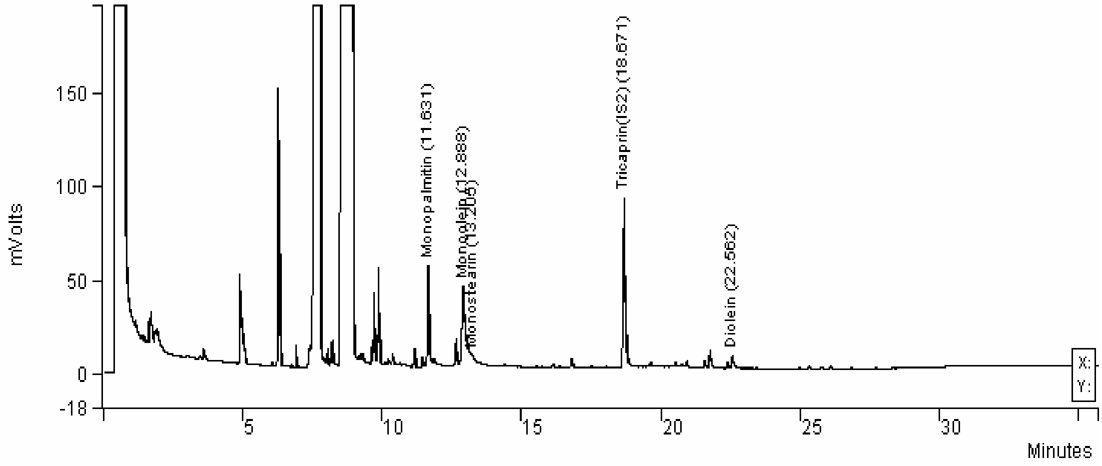
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	Monopalmitin	9.9013	11.632	-0.057	97321	0.00	BV	3.7		0
2	Monoolein	17.5488	12.897	-0.092	172490	0.00	PB	9.2		0
3	Tricaprin(IS2)	56.2642	18.663	-0.070	553027	0.00	BB	4.3		0
4	Diolein	5.2164	22.544	-0.052	51273	0.00	VB	4.8		0
	Totals	**88.9307**		**-0.271**	**874111**					

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	Monopalmitin	9.7207	11.645	-0.044	84962	0.00	BB	3.7		0
2	Monoolein	18.7754	12.917	-0.072	164101	0.00	PB	9.4		0
3	Tricaprin(IS2)	57.0373	18.664	-0.069	498520	0.00	BB	4.6		0
4	Diolein	5.1741	22.554	-0.042	45223	0.00	VB	4.7		0
	Totals	**90.7075**		**-0.227**	**792806**					

Figure A25 GC chromatogram of adsorbent dosage onto monoglyceride adsorption (10%DDM1.5)

Data File: c:\star\joe\default sample 3;51;41
Channel: Front = FID RESULTS
Sample ID: Default Sample
Operator (Inj): io
Injection Date: 08/02/2010 15:51:41
Injection Method: c:\star\en14105.mth
Run Time (min): 35.775
Workstation:
Instrument (Inj): gc

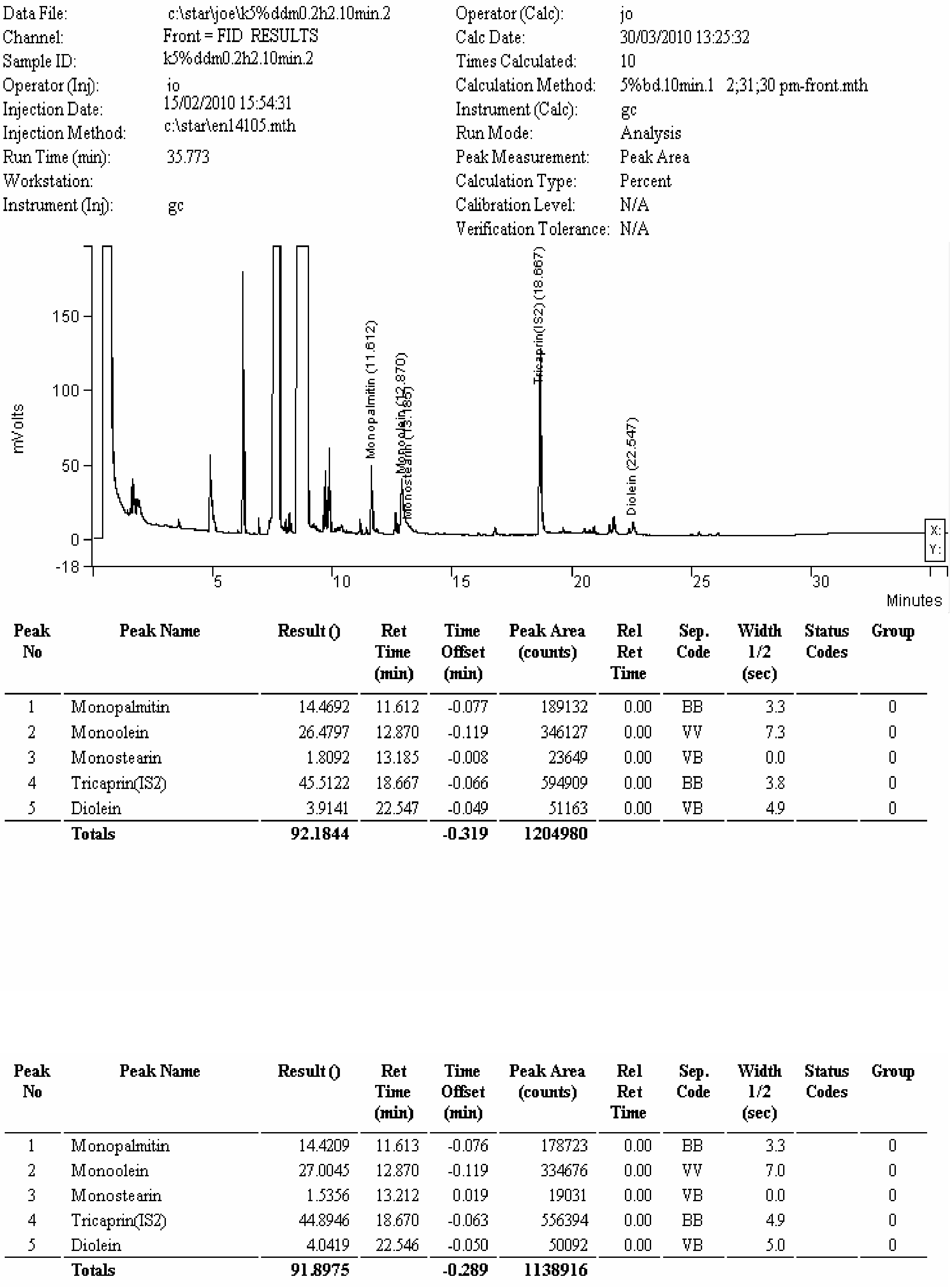
Operator (Calc): jo
Calc Date: 30/03/2010 12:29:54
Times Calculated: 7
Calculation Method: 5%bd.10min.1 2;31;30 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



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	Monopalmitin	19.3574	11.631	-0.058	231245	0.00	BB	3.4		0
2	Monoolein	32.6040	12.888	-0.101	389490	0.00	VV	6.9		0
3	Monostearin	2.4172	13.205	0.012	28877	0.00	VB	0.0		0
4	Tricaprin(IS2)	36.2908	18.671	-0.062	433533	0.00	BB	4.0		0
5	Diolein	2.8144	22.562	-0.034	33621	0.00	VB	3.9		0
	Totals	**93.4838**		**-0.243**	**1116766**					

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	Monopalmitin	17.0867	11.635	-0.054	209150	0.00	BB	3.4		0
2	Monoolein	33.7413	12.892	-0.097	413010	0.00	VV	6.7		0
3	Monostearin	1.9712	13.223	0.030	24129	0.00	VB	0.0		0
4	Tricaprin(IS2)	36.0299	18.684	-0.049	441025	0.00	BB	5.0		0
5	Diolein	2.8273	22.559	-0.037	34608	0.00	VV	4.4		0
	Totals	**91.6564**		**-0.207**	**1121922**					

Figure A26 GC chromatogram effect of $MnCl_2$ loading on natural diatomite for monoglyceride adsorption (untreated1)



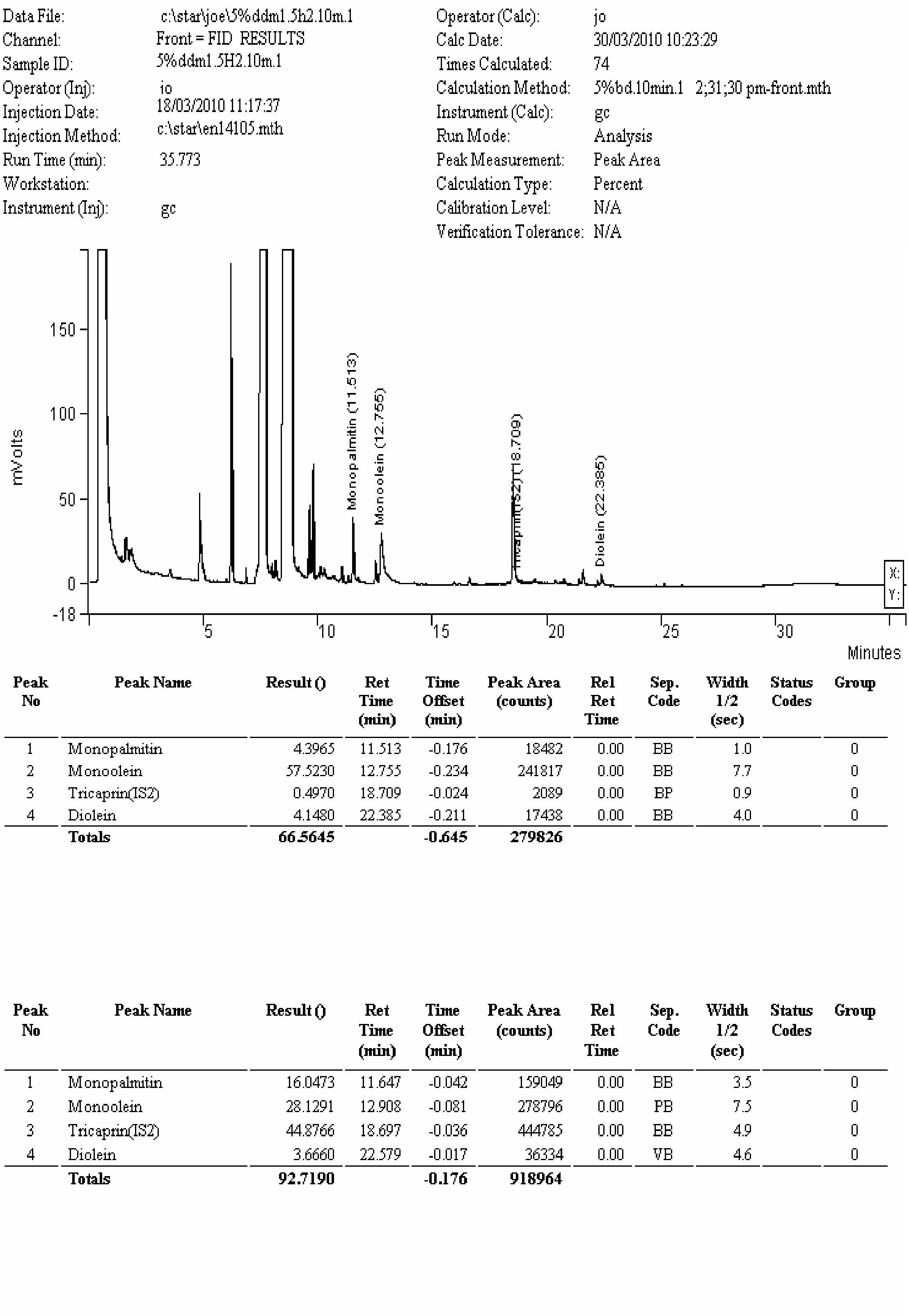
Data File: c:\star\joe\k5%ddm0.2h2.10min.2
Channel: Front = FID RESULTS
Sample ID: k5%ddm0.2h2.10min.2
Operator (Inj): jo
Injection Date: 15/02/2010 15:54:31
Injection Method: c:\star\en14105.mth
Run Time (min): 35.773
Workstation:
Instrument (Inj): gc

Operator (Calc): jo
Calc Date: 30/03/2010 13:25:32
Times Calculated: 10
Calculation Method: 5%bd.10min.1 2;31;30 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
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	Monopalmitin	14.4692	11.612	-0.077	189132	0.00	BB	3.3		0
2	Monoolein	26.4797	12.870	-0.119	346127	0.00	VV	7.3		0
3	Monostearin	1.8092	13.185	-0.008	23649	0.00	VB	0.0		0
4	Tricaprin(IS2)	45.5122	18.667	-0.066	594909	0.00	BB	3.8		0
5	Diolein	3.9141	22.547	-0.049	51163	0.00	VB	4.9		0
	Totals	**92.1844**		**-0.319**	**1204980**					

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	Monopalmitin	14.4209	11.613	-0.076	178723	0.00	BB	3.3		0
2	Monoolein	27.0045	12.870	-0.119	334676	0.00	VV	7.0		0
3	Monostearin	1.5356	13.212	0.019	19031	0.00	VB	0.0		0
4	Tricaprin(IS2)	44.8946	18.670	-0.063	556394	0.00	BB	4.9		0
5	Diolein	4.0419	22.546	-0.050	50092	0.00	VB	5.0		0
	Totals	**91.8975**		**-0.289**	**1138916**					

Figure A27 GC chromatogram effect of $MnCl_2$ loading on natural diatomite for monoglyceride adsorption (5%DDM0.2)



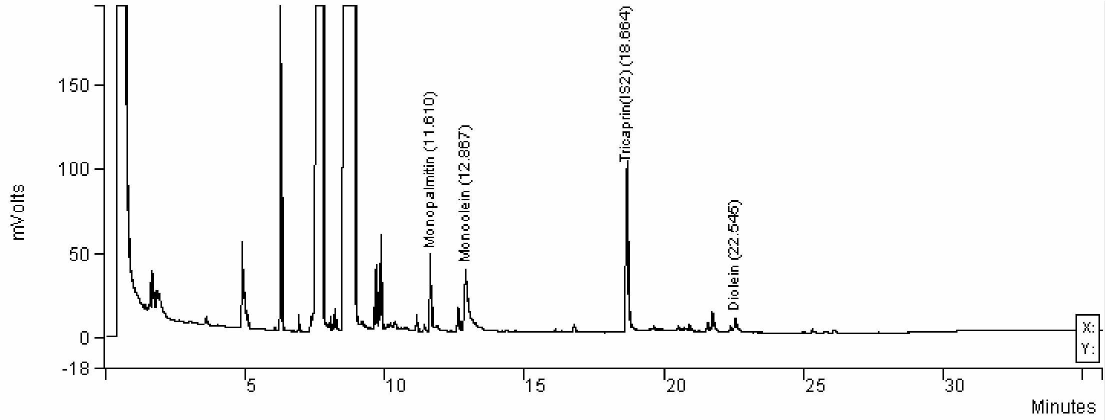
Data File:	c:\star\joe\5%ddml.5h2.10m.1	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	30/03/2010 10:23:29
Sample ID:	5%ddml.5H2.10m.1	Times Calculated:	74
Operator (Inj):	io	Calculation Method:	5%bd.10min.1 2;31;30 pm-front.mth
Injection Date:	18/03/2010 11:17:37	Instrument (Calc):	gc
Injection 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	Monopalmitin	4.3965	11.513	-0.176	18482	0.00	BB	1.0		0
2	Monoolein	57.5230	12.755	-0.234	241817	0.00	BB	7.7		0
3	Tricaprin(IS2)	0.4970	18.709	-0.024	2089	0.00	BP	0.9		0
4	Diolein	4.1480	22.385	-0.211	17438	0.00	BB	4.0		0
	Totals	**66.5645**		**-0.645**	**279826**					

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	Monopalmitin	16.0473	11.647	-0.042	159049	0.00	BB	3.5		0
2	Monoolein	28.1291	12.908	-0.081	278796	0.00	PB	7.5		0
3	Tricaprin(IS2)	44.8766	18.697	-0.036	444785	0.00	BB	4.9		0
4	Diolein	3.6660	22.579	-0.017	36334	0.00	VB	4.6		0
	Totals	**92.7190**		**-0.176**	**918964**					

Figure A28 GC chromatogram effect of $MnCl_2$ loading on natural diatomite for monoglyceride adsorption (5%DDM 1.5)

Data File:	c:\star\joe\k5%ddm2.5h2.10min.1	Operator (Calc):	jo
Channel:	Front = FID RESULTS	Calc Date:	15/02/2010 14:02:10
Sample ID:	K5%ddm2.5h2.10min.1	Times Calculated:	2
Operator (Inj):	io	Calculation Method:	i10%ddm1.5h2.10min. 10;55;17
Injection Date:	15/02/2010 12:56:09	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	Monopalmitin	15.0833	11.610	-0.079	191602	0.00	BB	3.3		0
2	Monoolein	29.1988	12.867	-0.122	370911	0.00	VB	7.4		0
3	Tricaprin(IS2)	42.7265	18.664	-0.069	542754	0.00	PB	4.9		0
4	Diolein	3.8702	22.545	-0.051	49163	0.00	VB	4.9		0
	Totals	**90.8788**		**-0.321**	**1154430**					

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	Monopalmitin	14.8836	11.612	-0.077	188820	0.00	BB	3.5		0
2	Monoolein	27.3525	12.868	-0.121	347004	0.00	VV	7.7		0
3	Monostearin	1.6614	13.208	0.015	21077	0.00	VB	0.0		0
4	Tricaprin(IS2)	43.1186	18.658	-0.075	547020	0.00	BB	3.9		0
5	Diolein	3.8184	22.546	-0.050	48442	0.00	VB	4.9		0
	Totals	**90.8345**		**-0.308**	**1152363**					

Figure A29 GC chromatogram effect of $MnCl_2$ loading on natural diatomite for monoglyceride adsorption (5%DDM 2.5)

APPENDIX B

Raw data of Characterized D&DDM and Raw data of adsorption process of D&DDM onto glycerin and monoglyceride removal

Table B1 Adsorption/ desorption isotherm of natural diatomite

Sample weight	3.89E-02	[g]	Saturated vapor pressure	97.198 [kPa]
Standard volume	9.043	[cm^3]	Adsorption cross sectionarea	0.162 [nm^2]
Dead volume	11.144	[cm^3 g^{-1}]	File name of walladsorption	
Equilibrium time	100	[sec]	Wall adsorption correction value 1	
Adsorptive	N2		Wall adsorption correction value 2	
Apparatus temperature	0	[C]	Number of adsorption data	29
Adsorption temperature	77	[K]	Number of desorption data	20

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}	
ADS							
1	0	0.5441	0	96.423	0.0056423	9.2132	
2	0	2.1802	0	96.476	0.022598	12.437	
3	0	3.9301	0	96.504	0.040725	13.732	
4	0	5.4892	0	96.544	0.056857	14.543	
5	0	6.9711	0	96.577	0.072182	15.149	
6	0	8.449	0	96.593	0.08747	15.707	
7	0	10.349	0	96.629	0.1071	16.398	
8	0	12.753	0	96.645	0.132	17.14	
9	0	14.275	0	96.69	0.1476	17.573	
10	0	15.729	0	96.718	0.1626	17.992	
11	0	17.637	0	96.73	0.1823	18.545	
12	0	21.38	0	96.759	0.221	19.573	
13	0	24.344	0	96.779	0.2515	20.346	
14	0	29.042	0	96.791	0.3	21.655	
15	0	33.877	0	96.827	0.3499	23.009	
16	0	38.676	0	96.827	0.3994	24.559	
17	0	43.881	0	96.86	0.453	26.412	
18	0	48.737	0	96.896	0.503	28.211	
19	0	53.495	0	96.965	0.5517	30.135	
20	0	58.408	0	96.997	0.6022	32.403	
21	0	63.252	0	96.997	0.6521	34.871	
22	0	68.059	0	97.029	0.7014	37.516	

Table B1 Adsorption/ desorption isotherm of natural diatomite (continues)

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}	
23	0	72.91	0	97.034	0.7514	40.344	
24	0	77.754	0	97.074	0.801	43.34	
25	0	82.508	0	97.114	0.8496	46.565	
26	0	87.62	0	97.151	0.9019	51.175	
27	0	92.37	0	97.199	0.9503	58.218	
28	0	94.77	0	97.244	0.9746	63.846	
29	0	96.499	0	97.276	0.992	70.267	
DES							
1	0	93.767	0	97.308	0.9636	64.824	
2	0	91.347	0	97.369	0.9382	60.923	
3	0	86.946	0	97.397	0.8927	55.752	
4	0	82.711	0	97.474	0.8485	52.071	
5	0	77.843	0	97.486	0.7985	48.825	
6	0	72.89	0	97.511	0.7475	46.217	
7	0	68.014	0	97.563	0.6971	44.025	
8	0	63.118	0	97.608	0.6466	42.152	
9	0	58.282	0	97.676	0.5967	40.355	
10	0	53.434	0	97.705	0.5469	38.526	
11	0	48.717	0	97.729	0.4985	36.136	
12	0	44.92	0	97.818	0.4592	28.203	
13	0	43.987	0	97.87	0.4494	27.284	
14	0	38.944	0	97.935	0.3977	24.654	
15	0	34.356	0	97.939	0.3508	23.165	
16	0	29.427	0	97.951	0.3004	21.749	
17	0	24.519	0	97.975	0.2503	20.383	
18	0	19.602	0	97.996	0.2	19.091	
19	0	14.71	0	98.012	0.1501	17.783	
20	0	9.8334	0	98.04	0.1003	16.314	

Table B2 BET plot of natural diatomite

Sample weight	3.89E-02	[g]	Saturated vapor pressure	97.198[kPa]
Standard volume	9.043	[cm^3]	Adsorption cross section area	0.162 [nm^2]
Dead volume	11.144	[cm^3 g^{-1}]	File name of walladsorption	
Equilibrium time	100	[sec]	Wall adsorption correction value 1	
Adsorptive	N2		Wall adsorption correction value 2	
Apparatus temperature	0	[C]	Number of adsorption data	29
Adsorption temperature	77	[K]	Number of desorption data	20

Starting point	6	
End point	15	
Slore	0.065461	
Intercept	0.00020595	
Correlation coefficient	0.9997	
Vm	15.228	[cm^3(STP) g^{-1}]
$a_{s,BET}$	66.281	[m^2 g^{-1}]
C	318.85	
Total pore volume (p/p_0=0.990)	0.1075	[cm^3 g^{-1}]
Average pore diameter	6.4862	[nm]

No	p/p_0	$p/V_a(p_0-p)$
1	0.0056423	0.00061589
2	0.022598	0.001859
3	0.040725	0.0030916
4	0.056857	0.0041453
5	0.072182	0.0051355
6	0.08747	0.0061027
7	0.1071	0.0073147
8	0.132	0.0088691
9	0.1476	0.0098565
10	0.1626	0.010794
11	0.1823	0.012024
12	0.221	0.014491
13	0.2515	0.016518
14	0.3	0.019795
15	0.3499	0.023389
16	0.3994	0.027082
17	0.453	0.03136

Table B3 Adsorption/desorption of DDM0.2

Sample weight	3.67E-02	[g]	Saturated vapor pressure	85.463[kPa]
Standard volume	9.043	[cm^3]	Adsorption cross section area	0.162 [nm^2]
Dead volume	10.666	[cm^3 g^{-1}]	File name of walladsorption	
Equilibrium time	100	[sec]	Wall adsorption correction value 1	
Adsorptive	N2		Wall adsorption correction value 2	
Apparatus temperature	0	[C]	Number of adsorption data	31
Adsorption temperature	77	[K]	Number of desorption data	19

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}	No
ADS							ADS
1	0	0.065122	0	85.242	0.00076397	10.574	1
2	0	0.814	0	85.226	0.0095514	16.099	2
3	0	1.6891	0	85.201	0.019825	17.78	3
4	0	3.3863	0	85.189	0.03975	19.526	4
5	0	4.8231	0	85.177	0.056624	20.555	5
6	0	6.15	0	85.161	0.072216	21.373	6
7	0	7.4443	0	85.141	0.087435	22.1	7
8	0	9.1171	0	85.133	0.1071	22.912	8
9	0	11.209	0	85.129	0.1317	23.825	9
10	0	12.569	0	85.12	0.1477	24.384	10
11	0	13.851	0	85.1	0.1628	24.889	11
12	0	15.523	0	85.096	0.1824	25.544	12
13	0	18.792	0	85.084	0.2209	26.715	13
14	0	21.405	0	85.076	0.2516	27.648	14
15	0	25.471	0	85.088	0.2993	29.061	15
16	0	29.7	0	85.092	0.349	30.518	16
17	0	34.36	0	85.104	0.4037	32.223	17
18	0	38.292	0	85.108	0.4499	33.668	18
19	0	42.492	0	85.112	0.4992	35.328	19
20	0	47.14	0	85.125	0.5538	37.224	20
21	0	51.406	0	85.161	0.6036	39.112	21
22	0	55.663	0	85.185	0.6534	41.198	22
23	0	59.908	0	85.222	0.703	43.518	23
24	0	64.125	0	85.238	0.7523	46.178	24
25	0	68.293	0	85.262	0.801	49.434	25
26	0	72.456	0	85.286	0.8496	53.67	26
27	0	76.478	0	85.306	0.8965	59.508	27
28	0	76.917	0	85.335	0.9014	60.304	28
29	0	82.001	0	85.383	0.9604	72.516	29

Table B3 Adsorption/desorption of DDM0.2 (continous)

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}	
DES							
1	0	82.55	0	85.529	0.9652	77.977	
2	0	80.609	0	85.581	0.9419	72.964	
3	0	76.002	0	85.642	0.8874	61.935	
4	0	72.77	0	85.699	0.8491	56.471	
5	0	68.423	0	85.751	0.7979	51.039	
6	0	64.308	0	85.775	0.7497	47.259	
7	0	59.961	0	85.824	0.6987	44.15	
8	0	55.635	0	85.836	0.6482	41.717	
9	0	51.316	0	85.868	0.5976	39.654	
10	0	47.03	0	85.905	0.5475	37.64	
11	0	42.7	0	85.945	0.4968	35.807	
12	0	38.434	0	85.965	0.4471	34.021	
13	0	34.124	0	86.002	0.3968	32.434	
14	0	29.858	0	86.042	0.347	30.844	
15	0	25.544	0	86.115	0.2966	29.339	
16	0	21.588	0	86.123	0.2507	27.9	
17	0	16.964	0	86.155	0.1969	26.223	
18	0	12.98	0	86.188	0.1506	24.691	
19	0	8.356	0	86.216	0.096919	22.719	

Table B 4 BET plot DDM0.2

Sample weight	3.67E-02	[g]
Standard volume	9.043	[cm^3]
Dead volume	10.666	[cm^3 g^{-1}]
Equilibrium time	100	[sec]
Adsorptive	N2	
Apparatus temperature	0	[C]
Adsorption temperature	77	[K]

Saturated vapor pressure	85.463[kPa]
Adsorption cross section area	0.162 [nm^2]
File name of walladsorption	
Wall adsorption correction value 1	
Wall adsorption correction value 2	
Number of adsorption data	31
Number of desorption data	19

Starting point	5	
End point	14	
Slore	0.047135	
Intercept	0.00019699	
Correlation coefficient	0.9998	
Vm	21.128	[cm^3(STP) g^{-1}]
$a_{s,BET}$	91.957	[m^2 g^{-1}]
C	240.27	
Total pore volume (p/p_0=0.990)	0.127	[cm^3 g^{-1}]
Average pore diameter	5.5235	[nm]

No	p/p_0	$p/V_a(p_0-p)$
1	0.00076397	0.000072305
2	0.0095514	0.00059901
3	0.019825	0.0011376
4	0.03975	0.00212
5	0.056624	0.0029201
6	0.072216	0.0036419
7	0.087435	0.0043354
8	0.1071	0.0052347
9	0.1317	0.0063646
10	0.1477	0.0071048
11	0.1628	0.0078108
12	0.1824	0.0087347
13	0.2209	0.010611
14	0.2516	0.012159
15	0.2993	0.014702
16	0.349	0.017569
17	0.4037	0.021014

Table B5 Adsorption/ desorption of DDM 1.5

Sample weight	3.79E-02 [g]	Saturated vapor pressure	86.287[kPa]
Standard volume	9.043 [cm^3]	Adsorption cross section area	0.162[nm^2]
Dead volume	11.273 [cm^3 g^{-1}]	File name of walladsorption	
Equilibrium time	100 [sec]	Wall adsorption correction value 1	
Adsorptive	N2	Wall adsorption correction value 2	
Apparatus temperature	0 [C]	Number of adsorption data	33
Adsorption temperature	77 [K]	Number of desorption data	22

No	pi /kPa	pe /kPa	$pe2$ /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}
ADS						
1	0	0.004064	0	85.733	0.000047403	10.997
2	0	0.1504	0	85.773	0.0017531	19.365
3	0	0.8575	0	85.806	0.0099934	24.656
4	0	1.9141	0	85.781	0.022314	27.226
5	0	3.686	0	85.818	0.042951	29.585
6	0	4.8117	0	85.797	0.056082	30.743
7	0	6.0959	0	85.81	0.07104	31.842
8	0	7.3964	0	85.81	0.086195	32.895
9	0	9.0626	0	85.818	0.1056	34.138
10	0	11.16	0	85.83	0.13	35.591
11	0	12.574	0	85.822	0.1465	36.516
12	0	13.874	0	85.83	0.1616	37.352
13	0	15.545	0	85.83	0.1811	38.421
14	0	19.145	0	85.842	0.223	40.719
15	0	21.458	0	85.862	0.2499	42.172
16	0	25.977	0	85.874	0.3025	45.103
17	0	30.268	0	85.89	0.3524	47.98
18	0	34.535	0	85.911	0.402	50.929
19	0	38.823	0	85.931	0.4518	53.966
20	0	43.119	0	85.943	0.5017	57.107
21	0	47.386	0	85.967	0.5512	60.449
22	0	51.669	0	85.996	0.6008	63.91
23	0	55.94	0	86.012	0.6504	67.604
24	0	60.248	0	86.024	0.7004	71.565
25	0	64.483	0	86.06	0.7493	75.907
26	0	69.059	0	86.121	0.8019	81.295
27	0	72.846	0	86.137	0.8457	86.957
28	0	73.35	0	86.174	0.8512	87.802

29	0	76.914	0	86.21	0.8922	94.957
30	0	77.764	0	86.242	0.9017	96.948
31	0	82.482	0	86.295	0.9558	110.76
32	0	84.055	0	86.327	0.9737	116.95
33	0	86.408	0	86.392	1.0002	127.59
DES						
1	0	82.701	0	86.44	0.9567	117.33
2	0	81.19	0	86.457	0.9391	113.21
3	0	76.918	0	86.505	0.8892	101.98
4	0	74.025	0	86.542	0.8554	95.59
5	0	73.566	0	86.57	0.8498	94.45
6	0	69.823	0	86.602	0.8063	87.739
7	0	69.254	0	86.622	0.7995	86.791
8	0	65.324	0	86.663	0.7538	81.063
9	0	64.853	0	86.683	0.7482	80.497
10	0	60.508	0	86.715	0.6978	75.633
11	0	56.135	0	86.768	0.647	71.46
12	0	52.071	0	86.804	0.5999	67.889
13	0	47.536	0	86.845	0.5474	63.766
14	0	43.411	0	86.889	0.4996	58.018
15	0	39.12	0	86.91	0.4501	54.112
16	0	34.657	0	86.934	0.3987	50.899
17	0	30.301	0	86.962	0.3484	47.856
18	0	25.932	0	86.998	0.2981	45.009
19	0	21.571	0	87.023	0.2479	42.25
20	0	17.215	0	87.031	0.1978	39.508
21	0	12.854	0	87.067	0.1476	36.759
22	0	8.514	0	87.1	0.09775	33.82

Table B6 BET plot DDM 1.5

Sample weight	3.79E-02	[g]
Standard volume	9.043	[cm^3]
Dead volume	11.273	[cm^3 g^{-1}]
Equilibrium time	100	[sec]
Adsorptive	N2	
Apparatus temperature	0	[C]
Adsorption temperature	77	[K]

Saturated vapor pressure	86.29
Adsorption cross section area	0.162
File name of walladsorption	
Wall adsorption correction value 1	
Wall adsorption correction value 2	
Number of adsorption data	33
Number of desorption data	22

Starting point	6	
End point	17	
Slore	0.031433	
Intercept	0.0001203	
Correlation coefficient	0.9998	
Vm	31.692	[cm^3(STP) g^{-1}]
$a_{s,BET}$	137.94	[m^2 g^{-1}]
C	262.31	
Total pore volume (p/p_0=0.990)	0.1909	[cm^3 g^{-1}]
Average pore diameter	5.5362	[nm]

No	p/p_0	$p/V_a(p_0-p)$
1	0.000047403	4.3107E-06
2	0.0017531	0.000090689
3	0.0099934	0.0004094
4	0.022314	0.00083828
5	0.042951	0.001517
6	0.056082	0.0019326
7	0.07104	0.0024016
8	0.086195	0.0028675
9	0.1056	0.0034586
10	0.13	0.0041993
11	0.1465	0.004701
12	0.1616	0.005162
13	0.1811	0.0057565
14	0.223	0.0070494
15	0.2499	0.0079005
16	0.3025	0.0096156
17	0.3524	0.011342
18	0.402	0.013199

Table B 7 Adsorption/ desorption of DDM2.5

Sample weight	4.17E-02 [g]	Saturated vapor pressure	97.24[kPa]
Standard volume	9.043 [cm^3]	Adsorption cross section area	0.162[nm^2]
Dead volume	11.273 [cm^3 g^{-1}]	File name of walladsorption	
Equilibrium time	100 [sec]	Wall adsorption correction value 1	
Adsorptive	N2	Wall adsorption correction value 2	
Apparatus temperature	0 [C]	Number of adsorption data	30
Adsorption temperature	77 [K]	Number of desorption data	21

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}
ADS						
1	0	0.9758	0	96.468	0.010115	7.3668
2	0	2.1305	0	96.476	0.022083	8.1421
3	0	4.0577	0	96.557	0.042024	8.8883
4	0	5.5824	0	96.54	0.057825	9.2874
5	0	7.0583	0	96.581	0.073082	9.6622
6	0	8.5098	0	96.613	0.088081	9.9768
7	0	10.425	0	96.629	0.1079	10.36
8	0	12.811	0	96.662	0.1325	10.851
9	0	14.32	0	96.686	0.1481	11.144
10	0	15.771	0	96.706	0.1631	11.398
11	0	17.699	0	96.751	0.1829	11.734
12	0	21.48	0	96.771	0.222	12.457
13	0	24.419	0	96.799	0.2523	13.013
14	0	29.18	0	96.831	0.3013	13.876
15	0	34.011	0	96.815	0.3513	14.796
16	0	38.829	0	96.856	0.4009	15.752
17	0	43.679	0	96.856	0.451	16.685
18	0	48.517	0	96.896	0.5007	17.643
19	0	53.372	0	96.896	0.5508	18.61
20	0	58.182	0	96.928	0.6003	19.678
21	0	62.992	0	96.989	0.6495	20.886
22	0	67.818	0	96.977	0.6993	22.312
23	0	73.014	0	97.021	0.7526	24.216
24	0	77.791	0	97.025	0.8018	26.616
25	0	82.475	0	97.054	0.8498	30.063
26	0	87.301	0	97.102	0.8991	36.411
27	0	91.245	0	97.143	0.9393	46.54
28	0	92.68	0	97.199	0.9535	52.506

Table B 7 Adsorption/ desorption of DDM2.5 (continues)

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}
DES						
1	0	93.782	0	97.381	0.963	70.487
2	0	92.278	0	97.474	0.9467	63.944
3	0	86.647	0	97.519	0.8885	44.004
4	0	83.512	0	97.604	0.8556	36.924
5	0	82.882	0	97.632	0.8489	35.922
6	0	78.304	0	97.672	0.8017	30.393
7	0	77.86	0	97.692	0.797	30.007
8	0	73.128	0	97.713	0.7484	26.8
9	0	68.143	0	97.749	0.6971	24.589
10	0	63.211	0	97.826	0.6462	22.986
11	0	58.723	0	97.846	0.6002	21.754
12	0	53.803	0	97.87	0.5497	20.597
13	0	48.936	0	97.899	0.4999	19.493
14	0	43.858	0	97.927	0.4479	17.112
15	0	39.186	0	97.951	0.4001	15.892
16	0	34.218	0	97.959	0.3493	14.925
17	0	29.302	0	97.979	0.2991	13.986
18	0	24.407	0	98.004	0.249	13.071
19	0	19.5	0	98.02	0.1989	12.146
20	0	14.6	0	98.036	0.1489	11.234
21	0	9.697	0	98.064	0.098884	10.313

Table B 8 BET plot DDM 2.5

Sample weight	4.17E-02	[g]
Standard volume	9.043	[cm^3]
Dead volume	11.273	[cm^3 g^{-1}]
Equilibrium time	100	[sec]
Adsorptive	N2	
Apparatus temperature	0	[C]
Adsorption temperature	77	[K]

Saturated vapor pressure	97.24
Adsorption cross section area	0.162
File name of walladsorption	
Wall adsorption correction value 1	
Wall adsorption correction value 2	
Number of adsorption data	30
Number of desorption data	21

Starting point	4	
End point	15	
Slore	0.1011	
Intercept	0.00067728	
Correlation coefficient	0.9998	
Vm	9.8237	[cm^3(STP) g^{-1}]
$a_{s,BET}$	42.757	[m^2 g^{-1}]
C	150.3	
Total pore volume (p/p_0=0.990)	0.1208	[cm^3 g^{-1}]
Average pore diameter	11.299	[nm]

No	p/p_0	$p/V_a(p_0-p)$
1	0.010115	0.0013871
2	0.022083	0.0027735
3	0.042024	0.0049354
4	0.057825	0.0066083
5	0.073082	0.00816
6	0.088081	0.0096814
7	0.1079	0.011673
8	0.1325	0.01408
9	0.1481	0.015601
10	0.1631	0.017096
11	0.1829	0.019081
12	0.222	0.022902
13	0.2523	0.025926
14	0.3013	0.031085
15	0.3513	0.036601
16	0.4009	0.042481
17	0.451	0.049229

Table B 9 Adsorption/ Desorption Activated charcoal

Sample weight	3.30E-02	[g]	Saturated vapor pressure	86.247	[kPa]
Standard volume	9.043	[cm^3]	Adsorption cross section area	0.162	[nm^2]
Dead volume	12.26	[cm^3 g^{-1}]	File name of walladsorption		
Equilibrium time	100	[sec]	Wall adsorption correction value 1		
Adsorptive	N2		Wall adsorption correction value 2		
Apparatus temperature	0	[C]	Number of adsorption data	50	
Adsorption temperature	77	[K]	Number of desorption data	18	

No	*pi* /kPa	*pe* /kPa	*pe*2 /kPa	p_0 /kPa	p/p_0	V_a/cm^3(STP) g^{-1}
ADS						
1	0	0.016296	0	85.745	0.00019005	12.707
2	0	0.020371	0	85.773	0.0002375	23.548
3	0	0.020371	0	85.802	0.00023742	34.392
4	0	0.024445	0	85.793	0.00028493	45.221
5	0	0.020371	0	85.785	0.00023747	56.059
6	0	0.032593	0	85.802	0.00037986	66.862
7	0	0.028519	0	85.802	0.00033238	77.691
8	0	0.028519	0	85.814	0.00033234	88.457
9	0	0.028519	0	85.822	0.0003323	99.205
10	0	0.024445	0	85.81	0.00028487	110.06
11	0	0.028519	0	85.842	0.00033223	120.77
12	0	0.028519	0	85.834	0.00033226	131.53
13	0	0.028519	0	85.846	0.00033221	142.31
14	0	0.032593	0	85.83	0.00037974	153.01
15	0	0.048889	0	85.842	0.00056952	163.62
16	0	0.061112	0	85.858	0.00071178	174.15
17	0	0.1059	0	85.874	0.0012336	184.43
18	0	0.2159	0	85.886	0.0025141	193.93
19	0	0.4074	0	85.915	0.004742	202.37
20	0	0.6885	0	85.927	0.0080128	209.34
21	0	1.0185	0	85.935	0.011852	214.49
22	0	1.5685	0	85.963	0.018246	220.22
23	0	1.7478	0	85.979	0.020328	221.61
24	0	2.6685	0	86	0.031029	227.03
25	0	3.5241	0	86.028	0.040965	230.43
26	0	4.8441	0	86.056	0.05629	233.9
27	0	6.2334	0	86.097	0.0724	236.31
28	0	7.3415	0	86.117	0.08525	237.73

29	0	9.0119	0	86.129	0.1046	239.41
30	0	11.183	0	86.141	0.1298	241.01
31	0	12.634	0	86.157	0.1466	241.89
32	0	13.97	0	86.174	0.1621	242.53
33	0	15.669	0	86.21	0.1818	243.29
34	0	19.026	0	86.218	0.2207	244.49
35	0	21.711	0	86.23	0.2518	245.27
36	0	25.976	0	86.246	0.3012	246.26
37	0	30.332	0	86.271	0.3516	247.03
38	0	34.667	0	86.295	0.4017	247.73
39	0	39.01	0	86.303	0.452	248.29
40	0	43.357	0	86.331	0.5022	248.74
41	0	47.696	0	86.347	0.5524	249.17
42	0	52.034	0	86.36	0.6025	249.53
43	0	56.369	0	86.388	0.6525	249.84
44	0	60.712	0	86.412	0.7026	250.17
45	0	65.051	0	86.432	0.7526	250.51
46	0	69.386	0	86.457	0.8025	250.8
47	0	73.607	0	86.465	0.8513	251.08
48	0	78.031	0	86.493	0.9022	251.52
49	0	83.841	0	86.501	0.9692	252.09
50	0	87.381	0	86.509	1.0101	252.54
DES						
1	0	82.289	0	86.529	0.951	252.23
2	0	76.247	0	86.55	0.881	251.97
3	0	73.379	0	86.566	0.8477	251.9
4	0	69.097	0	86.582	0.7981	251.74
5	0	64.795	0	86.606	0.7482	251.62
6	0	60.468	0	86.635	0.698	251.51
7	0	56.17	0	86.663	0.6481	251.35
8	0	51.863	0	86.683	0.5983	251.15
9	0	47.602	0	86.703	0.549	250.64
10	0	43.145	0	86.724	0.4975	249.02
11	0	38.936	0	86.756	0.4488	248.53
12	0	34.618	0	86.764	0.399	247.94
13	0	30.295	0	86.808	0.349	247.31
14	0	25.985	0	86.817	0.2993	246.55
15	0	21.678	0	86.845	0.2496	245.61
16	0	17.4	0	86.869	0.2003	244.36
17	0	12.829	0	86.897	0.1476	242.46
18	0	8.5515	0	86.93	0.098372	239.6

Table B 10 BET plot AC

The advantage over conventional water washing process is no wastewater generated from this adsorption process.

Sample weight	3.30E-02	[g]
Standard volume	9.043	[cm^3]
Dead volume	12.26	[cm^3 g^{-1}]
Equilibrium time	100	[sec]
Adsorptive	N2	
Apparatus temperature	0	[C]
Adsorption temperature	77	[K]

Saturated vapor pressure	86.247	[kPa
Adsorption cross section area	0.162	[nm^2
File name of walladsorption		
Wall adsorption correction value 1		
Wall adsorption correction value 2		
Number of adsorption data	50	
Number of desorption data	18	

The advantage over conventional water washing process is no wastewater generated from this adsorption process.

Starting point	6	
End point	26	
Slore	0.0045	
Intercept	2E-06	
Correlation coefficient	0.9999	
Vm	222.2	[cm^3(STP) g^{-1}]
$a_{s,BET}$	967.13	[m^2 g^{-1}]
C	2560.7	
Total pore volume (p/p_0=0.990)	0.39	[cm^3 g^{-1}]
Average pore diameter	1.6132	[nm]

No	p/p_0	$p/V_a(p_0-p)$	No	p/p_0	$p/V_a(p_0-p)$
1	0.00019	1.496E-05	22	0.018246	8.439E-05
2	0.000238	1.009E-05	23	0.020328	9.363E-05
3	0.000237	6.905E-06	24	0.031029	0.0001411
4	0.000285	6.303E-06	25	0.040965	0.0001854
5	0.000237	4.237E-06	26	0.05629	0.000255
6	0.00038	5.684E-06	27	0.0724	0.0003303
7	0.000332	4.28E-06	28	0.08525	0.000392
8	0.000332	3.758E-06	29	0.1046	0.0004881
9	0.000332	3.351E-06	30	0.1298	0.000619
10	0.000285	2.589E-06	31	0.1466	0.0007104
11	0.000332	2.752E-06	32	0.1621	0.0007978
12	0.000332	2.527E-06	33	0.1818	0.000913
13	0.000332	2.335E-06	34	0.2207	0.0011582
14	0.00038	2.483E-06	35	0.2518	0.001372
15	0.00057	3.483E-06	36	0.3012	0.0017502
16	0.000712	4.09E-06	37	0.3516	0.002195
17	0.001234	6.697E-06	38	0.4017	0.0027105
18	0.002514	1.3E-05	39	0.452	0.0033222
19	0.004742	2.354E-05			
20	0.008013	3.859E-05			
21	0.011852	5.592E-05			

Table B 11 Effect of temperature on precipitation of glycerin

Time (min	temp	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)
15	crude biodiesel	0.53	4.5	25121.6151
	50 open*	0.98	4.1	12378.5192
	50 close	0.8	4.1	15163.6860
	40 open	0.83	4.1	14615.6010
	40 close	0.81	3.6	13150.0800
	60 open	0.82	3.8	13711.3639
	60 close	0.82	3.1	11185.5863
	RT open	1.16	3.95	10075.1152
	RT close	1.01	3.4	9960.2091
50	50 open	1.56	2.8	5310.6092
	50 close	1.6	3	5547.6900
	40 open	1.52	2.45	4769.0668
	40 close	1.5	3.2	6312.0384
	60 open	1.5	2.8	5523.0336
	60 close	1.49	3	5957.2510
	RT open	1.62	3.05	5570.5200
	RT close	1.52	3	5839.6737
90	50 open	1.5	2.35	4482.7973
	50 close	1.55	3	5538.1161
	40 open	1.51	2.4	4547.8570
	40 close	1.51	2.5	4737.3510
	60 open	1.5	2.25	4292.0400
	60 close	1.53	2.25	4207.8824
	RT open	1.54	2.2	4087.6571
	RT close	1.5	2.6	4959.6907
180	50 open	1.5	1.8	3433.6320
	50 close	1.51	2.65	5021.5921
	40 open	1.5	2.2	4196.6613
	40 close	1.53	2.5	4675.4248
	60 open	2.19	2	2613.1142
	60 close	1.53	1.75	3272.7974
	RT open	1.56	1	1834.2051
	RT close	1.51	1.75	3316.1457

** Example for glycerin calculation see in appendix C*

Table B 12 Effect of contact time on glycerin adsorption

time	type of adsorbent	experiment	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	soap (g)	stdev
0	crude biodiesel	1	3	6	4992.16	0.004992	1.1727E-05
		2	3.01	6	4975.575	0.004976	
		average	3.005	6	4983.854	0.004984	
	control	1	3	4.5	3744.12	0.003744	8.7956E-06
		2	3.01	4.5	3731.681	0.003732	
		average	3.005	4.5	3737.89	0.003738	
10	D	D1	3.04	3.6	2955.884	0.002956	0.000109603
		D2	3.03	3.4	2800.882	0.002801	
		average	3.035	3.5	2878.511	0.002879	
	AC	AC1	3.08	3.8	3079.579	0.003080	0.000174554
		AC2	3.04	3.45	2832.722	0.002833	
		average	3.06	3.625	2956.958	0.002957	
20	D	1	3.02	3.3	2727.505	0.002728	6.4615E-05
		2	3.03	3.2	2636.124	0.002636	
		average	3.025	3.25	2681.739	0.002682	
	AC	1	3.01	3.15	2612.177	0.002612	6.1162E-06
		2	3.02	3.15	2603.527	0.002604	
		average	3.015	3.15	2607.845	0.002608	
30	D	1	3.02	3.1	2562.201	0.002562	0.000105
		2	3	2.9	2412.877	0.002413	
		average	3.01	3	2487.787	0.002488	
	AC	1	3.18	3	2354.792	0.002355	9.4407E-05
		2	3.21	3.2	2488.304	0.002488	
		average	3.195	3.1	2421.862	0.002422	

Table B 13 Effect of concentration of adsorption on glycerin adsorption

Type of adsorbent& %adsorbent	No.	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	%adsorb	Stdev
crude biodiesel	1	3	4.5	4155.06	0	0
	2	3	4.5	4155.06		
	average	3	4.5	4155.06		
1%AC	1	3.02	2.5	2293.079	45.5555	0.0001959
	2	3.01	2.4	2208.67		
	average	3.015	2.45	2250.945		
2%AC	1	3.05	2.35	2134.293	47.2222	9.793E-05
	2	3.06	2.4	2172.58		
	average	3.055	2.375	2153.468		
3%AC	1	3.07	2	1804.586	54.4444	0.0001958
	2	3.07	2.1	1894.816		
	average	3.07	2.05	1849.701		
4%AC	1	3.02	1.8	1651.017	58.8889	0.0001958
	2	3.06	1.9	1719.959		
	average	3.04	1.85	1685.715		
5%AC	1	3.05	1.8	1634.778	60.5556	9.79357E-05
	2	3.06	1.75	1584.173		
	average	3.055	1.775	1609.434		
crude biodiesel	1	3.02	5.5	5044.775	0	0.0001958
	2	3.01	5.4	4969.507		
	average	3.015	5.45	5007.203		
1%D	1	3.12	2.85	2530.325	48.16514	9.79357E-05
	2	3.11	2.8	2493.927		
	average	3.115	2.825	2512.155		
2%D	1	3.07	2.85	2571.536	49.54128	0.0003917
	2	3	2.65	2446.869		
	average	3.035	2.75	2509.921		
3%D	1	3.06	2.65	2398.891	53.21101	0.0003917
	2	3	2.45	2262.199		
	average	3.03	2.55	2331.222		
4%D	1	3.03	2.1	1919.83	61.46789	0.0008814
	2	3	2	1846.693		
	average	3.015	2.1	1929.381		
5%D	1	3.04	2	1822.395	61.92661	0.0001959
	2	3.06	2.15	1946.27		
	average	3.1	2.075	1854.14		
control	1	3.6	3.7	2846.986	87.22222	0.003183
	2	3	4.15	3831.889		
	average	3.3	3.925	3294.669		

Table B 14 Effect of methanol removal on glycerin adsorption

Natural diatomite weight of oil sample 35 concentration of HCl = 0.0091 mole						
Concentration of adsorbent to oil,wt (%)	No.	weight of adsorbent	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	Stdev
demethanol crude biodiesel	1	0	3.04	5.45	1052.6152	0
	2	0	5	1.9	1052.6152	
	average	0	5	1.9	1052.6152	
0.2	1	0.07	5	1.9	1052.6152	0.01922
	2	0.07	10.09	0.1	27.4533	
	average	0.07	10.1	0.1	27.4261	
0.4	1	0.14	10.095	0.1	27.4397	0.042596
	2	0.14	14.37	0.15	28.9148	
	average	0.14	14.4	0.15	28.8546	
0.6	1	0.21	14.385	0.15	28.8847	0.027555
	2	0.21	17.87	0.15	23.2516	
	average	0.21	17.9	0.15	23.2126	
0.8	1	0.28	17.885	0.15	23.2321	0.008571
	2	0.28	18.52	0.15	22.4355	
	average	0.28	18.51	0.15	22.4476	
1.0	1	0.35	18.515	0.15	22.4416	0.007036
	2	0.35	20.43	0.15	20.3380	
	average	0.35	20.44	0.15	20.3281	

Table B15 Breakthrough point and capacity of natural diatomite on glycerin adsorption

	Added crude biodiesel, (g)	Total added biodiesel, (g)	experiment	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	C/Co	Stdev
	demethanol crude biodiesel	-	1	12.65	0.9	197.0779	197.0779	0.1102
			2	12.64	0.9	197.2339	197.2339	
			average	12.65	0.9	197.0779	197.0779	
1	30	30	1	10	0	0.0000	0	0.0000
			2	10	0	0.0000	0	
			average	10	0	0.0000	0	
2	30	60	1	10	0	0.0000	0	0.0000
			2	10	0	0.0000	0.06401	
			average	10	0	0.0000	0.1382	
3	30	90	1	10	0	0.0000	0.2039	0.0000
			2	10	0	0.0000	0.3200	
			average	10	0	0.0000	0.3333	
4	30	120	1	10	0	0.0000	0.4667	0.0000
			2	10	0	0.0000	0.5561	
			average	10	0	0.0000	0.5698	
5	30	150	1	10.98	0.05	12.6140	0.6159	0.0081
			2	10.99	0.05	12.6025	0.6153	
			average	10.985	0.05	12.6083	0.6171	
6	30	180	1	10.17	0.1	27.2374	0.6099	0.0095
			2	10.175	0.1	27.2240	0.6165	
			average	10.1725	0.1	27.2307	0.5889	
7	30	210	1	10.34	0.15	40.1843	0.5911	0.0275
			2	10.35	0.15	40.1455	0.6018	
			average	10.345	0.15	40.1649	0.6030	
8	30	240	1	10.98	0.25	63.0701	0.6035	0.0407
			2	10.97	0.25	63.1276	0.6053	
			average	10.975	0.25	63.0989	0.6207	
9	30	270	1	12.65	0.3	65.6926	0.6219	0.7369
			2	12.66	0.305	66.7348	0.6275	
			average	12.655	0.3025	66.2139	0.6458	
10	30	300	1	10.54	0.35	91.9843	0.6477	
			2	10.56	0.35	91.8100	0.6477	0.1232
			average	10.54	0.35	91.9843	0.6477	
11	30	330	1	10.11	0.4	109.5960	0	0.0766
			2	10.12	0.4	109.4877	0	
			average	10.115	0.4	109.5419	0	
12	30	360	1	11.1	0.45	112.2989	0	
			2	11.05	0.45	112.8071	0.06401	0.1801
			average	11.075	0.45	112.5524	0.1382	
13	30	390	1	10.27	0.45	121.3747	0.2039	0.0836
			2	10.26	0.45	121.4930	0.3200	
			average	10.265	0.45	121.4338	0.3333	

Table B15 Breakthough and capacity of natural diatomite on glycerin adsorption (2)

No.	Added crude biodiesel, (g)	Total added biodiesel, (g)	experiment	weigh sampling crude biodiesel(g)	Titrant, B (ml)	Soap (ppm)	C/Co	Stdev
14	30	420	1	10.28	0.45	121.2566	0.4667	0.1253
			2	10.265	0.45	121.4338	0.5561	
			average	10.2725	0.45	121.3451	0.5698	
15	30	450	1	10.25	0.45	121.6115	0.6159	0.0840
			2	10.24	0.45	121.7303	0.6153	
			average	10.245	0.45	121.6709	0.6171	
16	30	480	1	10.37	0.45	120.2042	120.2042	0.0820
			2	10.36	0.45	120.3203	120.3203	
			average	10.365	0.45	120.2622	120.2622	
17	30	510	1	10.26	0.45	121.4930	121.4930	0.0836
			2	10.27	0.45	121.3747	121.3747	
			average	10.265	0.45	121.4338	121.4338	
18	30	540	1	10.74	0.45	116.0631	116.0631	0.0765
			2	10.73	0.45	116.1713	116.1713	
			average	10.735	0.45	116.1172	116.1172	
19	30	570	1	10.7	0.45	116.4970	116.4970	0.0769
			2	10.71	0.45	116.3882	116.3882	
			average	10.705	0.45	116.4426	116.4426	
20	30	600	1	10.51	0.45	118.6030	118.6030	0.0799
			2	10.5	0.45	118.7160	118.7160	
			average	10.505	0.45	118.6595	118.6595	
21	30	630	1	10.49	0.45	118.8292	118.8292	0.0802
			2	10.48	0.45	118.9426	118.9426	
			average	10.485	0.45	118.8858	118.8858	
22	30	660	1	10.48	0.45	118.9426	118.9426	0.0802
			2	10.49	0.45	118.8292	118.8292	
			average	10.485	0.45	118.8858	118.8858	
23	30	690	1	10.45	0.45	119.2840	119.2840	0.0808
			2	10.44	0.45	119.3983	119.3983	
			average	10.445	0.45	119.3411	119.3411	
24	30	720	1	10.19	0.45	122.3276	122.3276	0.0850
			2	10.18	0.45	122.4477	122.4477	
			average	10.185	0.45	122.3876	122.3876	
25	30	750	1	10.17	0.45	122.5681	122.5681	0.0853
			2	10.16	0.45	122.6888	122.6888	
			average	10.165	0.45	122.6284	122.6284	
26	30	780	1	10.08	0.45	123.6625	123.6625	0.0868
			2	10.07	0.45	123.7853	123.7853	
			average	10.075	0.45	123.7239	123.7239	
27	30	810	1	11.97	0.55	127.2784	127.2784	0.0751
			2	11.98	0.55	127.1721	127.1721	
			average	11.975	0.55	127.2252	127.2252	
28	30	840	1	10.85	0.5	127.6516	127.6516	0.0833
			2	10.84	0.5	127.7694	127.7694	
			average	10.845	0.5	127.7105	127.7105	

Table B15 Breakthough and capacity of natural diatomite on glycerin adsorption (3)

	Added crude biodiesel, (g)	Total added biodiesel, (g)	experiment	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	C/Co	Stdev
29	30	870	1	10.85	0.5	127.6516	127.6516	0.0831
			2	10.86	0.5	127.5341	127.5341	
			average	10.855	0.5	127.5928	127.5928	
30	30	900	1	10.85	0.5	127.6516	127.6516	0.0833
			2	10.84	0.5	127.7694	127.7694	
			average	10.845	0.5	127.7105	127.7105	

Table B 16 Adsorption isotherm of glycerin

crude biodiesel (density = 0.88g/ml) weight 20g , so volume = 20x0.88=22.7ml concentration of HC l=0.0092 mole/L					
weight of adsorbent (g)	Experiment	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	Stdev
crude biodiesel	1	3.01	5.05	4698.4797	86.2802
	2	3.05	5.25	4820.4984	
	average	3.03	5.15	4759.8917	
0.1	1	5.52	4.75	2409.8333	21.0621
	2	5.51	4.8	2439.6196	
	average	5.515	4.775	2424.7130	
0.2	1	4.51	3.65	2266.4639	3.5614
	2	4.5	3.65	2271.5004	
	average	4.505	3.65	2268.9794	
0.3	1	5.04	3.85	2139.2556	2.9954
	2	5.05	3.85	2135.0194	
	average	5.045	3.85	2137.1354	
0.4	1	5.2	3.7	1992.6492	16.2998
	2	5.21	3.75	2015.7006	
	average	5.205	3.725	2004.1860	
0.5	1	4.22	2.8	1858.1384	3.1062
	2	4.23	2.8	1853.7456	
	average	4.225	2.8	1855.9394	
0.6	1	4.53	2.8	1730.9810	2.7079
	2	4.52	2.8	1734.8106	
	average	4.525	2.8	1732.8937	
0.7	1	5.83	3.45	1657.2309	14.9475
	2	5.84	3.5	1678.3699	
	average	5.835	3.475	1667.8094	

Table B 16 Adsorption isotherm of glycerin (2)

weight of adsorbent (g)	Experiment	weigh sampling crude biodiesel (g)	Titrant, B (ml)	Soap (ppm)	Stdev
0.8	1	4.49	2.55	1590.4731	19.5035
	2	4.5	2.6	1618.0551	
	average	4.495	2.575	1604.2794	
0.9	1	4.52	2.45	1517.9593	2.3800
	2	4.51	2.45	1521.3251	
	average	4.515	2.45	1519.6403	
1	1	3.98	2.1	1477.6402	2.6319
	2	3.97	2.1	1481.3622	
	average	3.975	2.1	1479.4989	

Table B16 Adsorption isotherm of glycerin (2)

weight of adsorbent (g)	Ce (mg/l)	adsorbet (mg/l) Co-Ce	x/m (mg/g)	log(x/m)	log (Ce)	1/Ce	1/(x/m)
0	Co=4759.8917	0	0				
0.1*	2424.7130	2335.1788	530.5526	3.3847	2.7247	0.000412	0.001885
0.2	2268.9794	2490.9124	282.9676	3.3558	2.4517	0.000441	0.003534
0.3	2137.1354	2622.7564	198.6301	3.3298	2.2980	0.000468	0.005034
0.4	2004.1860	2755.7058	156.5241	3.3019	2.1946	0.000499	0.006389
0.5	1855.9394	2903.9523	131.9556	3.2686	2.1204	0.000539	0.007578
0.6	1732.8937	3026.9980	114.6223	3.2388	2.0593	0.000577	0.008724
0.7	1667.8094	3092.0823	100.3602	3.2221	2.0016	0.0006	0.009964
0.8	1604.2794	3155.6123	89.6194	3.2053	1.9524	0.000623	0.011158
0.9	1519.6403	3240.2514	81.7983	3.1817	1.9127	0.000658	0.012225
1	1479.4989	3280.3929	74.5305	3.1701	1.8723	0.000676	0.013417

**example for furendlish and langmuir isotherm calculation see in appendix C*

Table B17 Effect of contact time on monoglyceride adsorption

Time (min.)	Name	Area1 uV.min	Area2 uV.min	Quanlitative average%(m/M)	Stdev
0	Monoglycerides	981536	1042408	1.24897	0.04244
	Tricaprin (IS2 0.8 mg)	437368	443361		
5	Monoglycerides	779983	776506	1.07196	0.01231
	Tricaprin (IS2 0.8 mg)	408484	400173		
10	Monoglycerides	795415	722215	0.98449	0.00934
	Tricaprin (IS2 0.8 mg)	446138	410498		
15	Monoglycerides	766087	798231	0.97952	0.09512
	Tricaprin (IS2 0.8 mg)	465484	423296		
20	Monoglycerides	671462	677780	0.97557	0.01178
	Tricaprin (IS2 0.8 mg)	385040	382151		

Table B18 Comparisons of various types of adsorbent on monoglyceride removal

Type of adsorbent	**Name 0min**	**Area1 uV.min**	**Area2 uV.min**	**Quanlitative average%(m/M)**	**Stdev**
untreated	Monoglycerides	981536	1042408	1.24897	0.04244
	Tricaprin (IS2 0.8 mg)	437368	443361		
5%d	Monoglycerides	859106	859106	1.20297	0
	Tricaprin (IS2 0.8 mg)	396539	396539		
5%ddm1.5	Monoglycerides	795415	722215	0.98449	0.00934
	Tricaprin (IS2 0.8 mg)	446138	410498		
5%BD	5%BD Monoglycerides	904345	950591	0.97952	0.07993
	Tricaprin (IS2 0.8 mg)	419367	403048		

Table B19 Effect of concentration of adsorbent on monoglyceride adsorption

%adsorbent, wt.	**Name**	**Area1 uV.min**	**Area2 uV.min**	**Quanlitative average%(m/M)**	**Stdev**
0%	Monoglycerides	649612	678304	0.8380	0.0153
	Tricaprin (IS2 0.8 mg)	433533	441279		
2%	Monoglycerides	509575	536937	0.5972	0.04336
	Tricaprin (IS2 0.8 mg)	521285	447188		
4%	Monoglycerides	478273	424773	0.4746	0.04176
	Tricaprin (IS2 0.8 mg)	521170	522903		
5%	Monoglycerides	260299	410749	0.3810	0.02893
	Tricaprin (IS2 0.8 mg)	392290	421784		
6%	Monoglycerides	400321	332916	0.3926	0.00890
	Tricaprin (IS2 0.8 mg)	547876	470085		
7%	Monoglycerides	327319	326014	0.3535	0.0193
	Tricaprin (IS2 0.8 mg)	487477	523369		
8%	Monoglycerides	284883	268543	0.3047	0.00155
	Tricaprin (IS2 0.8 mg)	505960	480268		
9%	Monoglycerides	237177	237874	0.2843	0.01074
	Tricaprin (IS2 0.8 mg)	441135	465845		
10%	Monoglycerides	280444	269811	0.2816	0.02654
	Tricaprin (IS2 0.8 mg)	505394	553027		

Table B 20 Effect of MnCl2 coating on natural diatomite for monoglyceride adsorption

Concentration 0f $MnCl_2$ doped on diatomite (mole/l)	**Name**	**Area1 uV.min**	**Area2 uV.min**	**Quanlitative average% (m/M)**	**Stdev**
untreat	Monoglycerides	649612	678304	0.8380	0.01530
	Tricaprin (IS2 0.8 mg)	433533	441279		
ddm 0.2	Monoglycerides	558908	532430	0.5196	0.00689
	Tricaprin (IS2 0.8 mg)	594909	559394		
ddm 1.5	Monoglycerides	260299	410749	0.3810	0.02893
	Tricaprin (IS2 0.8 mg)	392290	421784		
ddm2.5	Monoglycerides	562513	556901	0.5655	0.00727
	Tricaprin (IS2 0.8 mg)	542754	547020		

Table B21 Adsorption isotherm of monoglyceride

adsorbent (g)	(%mono)	Ce (g/l)	Adsorbet (mg/l)	x/m (g/g)	log(Ce)	log(x/m)	1/Ce	1/(x/m)
0	0.8380	8379.859	0	95.8800	3.6191	1.9817	0.00024	0.01043
0.25	0.4160	4159.79	4220.069	89.6661	3.5939	1.9526	0.000255	0.011152
0.3069	0.3926	3925.61	4844.813	78.4675	3.5484	1.8947	0.000283	0.012744
0.3507	0.3535	3535.046	4844.813	75.7130	3.484	1.8792	0.000328	0.013208
0.4	0.3048	3047.959	5331.9	69.8075	3.4538	1.8439	0.000352	0.014325
0.4505	0.2843	2843.192	5536.667	65.3322	3.4198	1.8151	0.00038	0.015306
0.5	0.2629	2628.783	5751.075	136.7905	3.7761	2.1361	0.000167	0.00731

APPENDIX C

Calculation methods

C 1. Calculated of glycerin content (ppm)

$$\text{g of glycerin /g of crude biodiesel} = \frac{\text{B x [HCl] x304.4}}{\text{W x 1000}}$$

where:

B = volume of hydrochloric acid used in step 2.

W = weight of crude biodiesel used (g).

Concentration of HCl = 0.00972 mole /L

Exaammple: Effect of temperature on precipitation of glycerin (50 open)

$$\boxed{\frac{\text{g of glycerin}}{\text{g of crude biodiesel}} = \frac{\text{4.5 ml X 0.00972 X 320.56}}{\text{100 X 0.53g}} = \text{25121.6151 ppm}}$$

C 2. Calculation of free and total glycerin calibration functions (Linear regression) (EN 14105)

C 2.1 Free Glycerol

Table C1 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 C2 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
$\Sigma X = 3.576$	$\Sigma Y = 2.750$	$\Sigma X^2 = 2.113$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.654$

$(\Sigma X)^2 = 12.787$ $(\Sigma Y)^2 = 7.563$ 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:

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

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

C 2.2 Monoglyceride

Table C 3 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 C 4 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
$\Sigma X = 11.007$	$\Sigma Y = 7.625$	$\Sigma X^2 = 18.707$	$\Sigma Y^2 = 9.023$	$\Sigma XY = 12.992$

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

$$a_m = \frac{(8\times 12.992) - (11.007\times 7.625)}{(8\times 18.707) - 58.141} = 0.7021$$

$$b_m = \frac{7.625 - (0.7021\times 11.007)}{8} = -0.1298$$

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

C 2.3 Diglyceride

Table C 5 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 C 6 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
$\Sigma X = 3.019$	$\Sigma Y = 2.750$	$\Sigma X^2 = 1.529$	$\Sigma Y^2 = 1.297$	$\Sigma XY = 1.408$

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

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

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

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

C 2.4 Triglyceride

Table C 7 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 C 8 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
$\Sigma X = 2.296$	$\Sigma Y = 2.250$	$\Sigma X^2 = 0.889$	$\Sigma Y^2 = 0.859$	$\Sigma XY = 0.874$

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

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

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

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

C 3 Example of calculated glycerol content (EN14105)

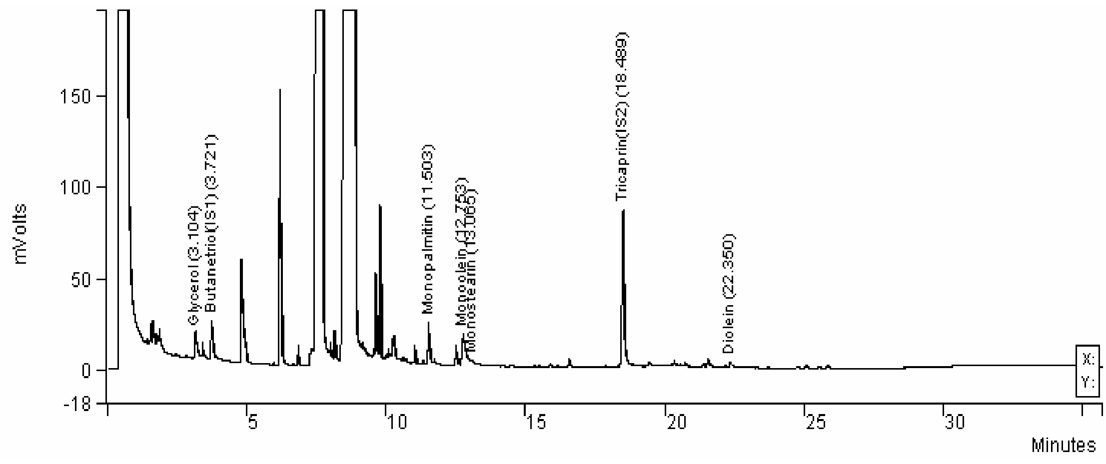
The percentage (m/m) of free glycerol in the sample was calculated by the following equation:

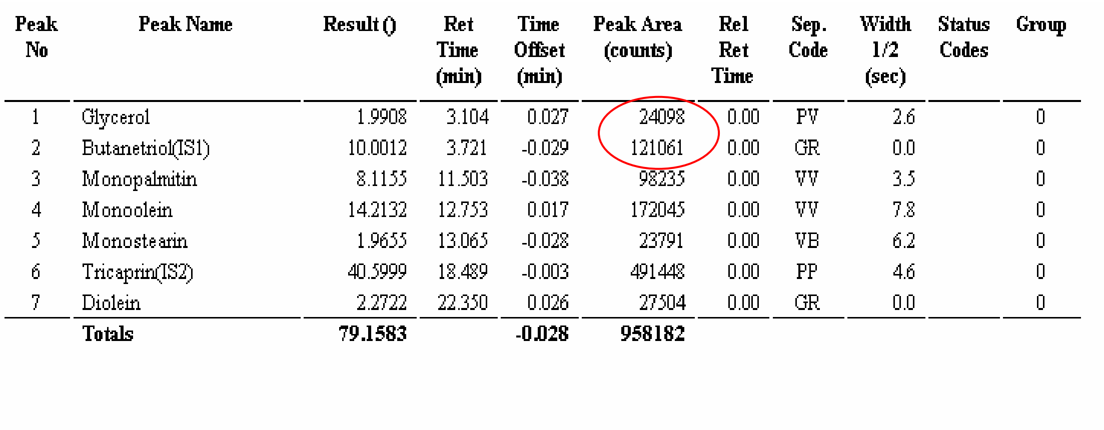
$$G = [a_g\,(A_g / A_{eil}) + b_g] \times (M_{eil} / m) \times 100$$

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

Sample: GC chromatogram of dry water-washing process with 4% natural diatomite for free removal 1





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	1.9908	3.104	0.027	24098	0.00	PV	2.6		0
2	Butanetriol(IS1)	10.0012	3.721	-0.029	121061	0.00	GR	0.0		0
3	Monopalmitin	8.1155	11.503	-0.038	98235	0.00	VV	3.5		0
4	Monoolein	14.2132	12.753	0.017	172045	0.00	VV	7.8		0
5	Monostearin	1.9655	13.065	-0.028	23791	0.00	VB	6.2		0
6	Tricaprin(IS2)	40.5999	18.489	-0.003	491448	0.00	PP	4.6		0
7	Diolein	2.2722	22.350	0.026	27504	0.00	GR	0.0		0
	Totals	**79.1583**		**-0.028**	**958182**					

$$G = [(0.8264 \times (24098/121061)) + (-0.02564)] \times (0.08/100) \times 100 = 0.01111 \text{ (m/m)}$$

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

$$M = [a_m (\Sigma A_{mi}/A_{ei2}) + b_m] \times (M_{ei2}/m) \times 100$$

$$D = [a_d (\Sigma A_{di}/A_{ei2}) + b_d] \times (M_{ei2}/m) \times 100$$

$$T = [a_t (\Sigma A_{ti}/A_{ei2}) + b_t] \times (M_{ei2}/m) \times 100$$

Where:

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

ΣA_{mi}, ΣA_{di}, ΣA_{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

$$M = \left(\left(0.702147 \text{ x } \frac{(98235+172045+23791)}{491448}\right) + (-0.01298)\right] \text{ x } \frac{(0.8)}{100} \text{ x } 100 = 0.3257$$

$$D = \left(\left(1.13201 \text{ x } \frac{(27504)}{491448}\right) + (-0.00727)\right] \text{ x } \frac{(0.8)}{100} \text{ x } 100 = 0.04486$$

$$T = \left(\left(0.96579 \text{ x } \frac{(\;\;0\;\;)}{491448}\right) + (-0.0149)\right] \text{ x } \frac{(0.8)}{100} \text{ x } 100 =- 0.01191$$

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:

GT = 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

GT =0.01111 +(0.255 x 0.3257) + (0.146 x 0.04486) +(0.103x -0.0149) = 0.09949

C 4 Calibration curve of Mn ion

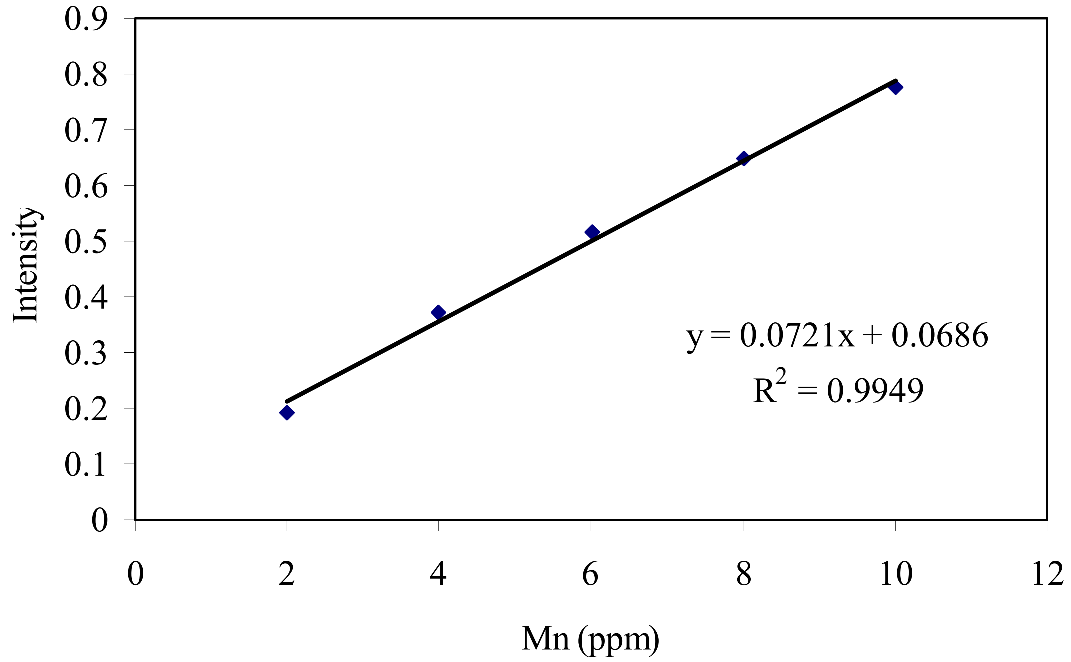


Figure C 1 Calibration curve of Mn

C 5 Adsorption isotherm of Fruendlich isotherm and Langmiur

$$\frac{X}{M} = \frac{(Co\text{-}Ce)Vs}{m}$$

Where :

X = mass of adsorbete (mg)

m = mass of adsorbent (g)

Co = initial concentration of adsorbete (mg/l)

Ce = adserbete concentration at equilibrium condition (mg/l)

Vs = volume of solution (L)

From Table B16 Adsorption isotherm of glycerin
Co= 4759.8917mg/l , Ce = 2424.7130mg/l , Vs = 0.0227 L , m = 0.1 g

$$\frac{X}{M} = \frac{(4759.8917 - 2424.7130) * 0.0227}{0.1}$$

$$= 530.5526 \text{ mg/g}$$

$$\text{Log } (x/m) = \log(530.5526)$$
$$= 3.3847$$

$$\text{Log Ce} = \text{Log}(2424.7130)$$
$$= 2.7247$$

$$1/\text{Ce} = 1/2424.7130$$
$$= 0.000412$$

$$1/(x/m) = 1/ 530.5526$$
$$= 0.001885$$

From Table 4.2

$$\text{RL} = 1/ (1+ (3.54*10\text{^}-4 *4759.8917))$$
$$= 0.3721$$

C 5.1 Freundlich isotherm of glycerin

When log(x/m) versus logCe was plotted See Figure 4.15), the intercept when Ce = 1.0 is the value of (x/m) and the slope of the line is equal to 1/n .

Thus, log(x/m) = 0.6864, and Kf = 0.7719 When log(x/m) = 1.0, logCe= 3.2149, and 1/n = 3.4601 Thus,

$$\text{Slope} = \frac{1}{n} = 3.4601$$

$$\text{Interception y} = \log K_f = -9.1609$$

$$K_f = 6.91*10\text{^}-10$$

From $x/m = K_f Ce^{1/n}$

$x/m = 6.91*10^{-10} * Ce^{3.4601}$

C 5.2 Langmuir isotherm of glycerin

When 1/Ce versus 1/(x/m) was plotted, the interception in 1/a and slope of the line is equal to 1 / (ab).

When

$1/a = -0.0146$

$a = -68.4931$

$\frac{1}{ab} = 41.174$

$b = \frac{1}{(41.174)*(-68.4931)}$

$b = 0.354*10^{-4}$

From $Ce/(x/m) = 1/(ab) + (1/a)C_e$

So, $x/m = (-68.4931 x -0.354 x 10^{-4} Ce) / (1+(-0.354*10^{-4})Ce)$

The important characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L [17]

$R_L = 1/(1+bCo)$

$R_L = \frac{1}{(1 + (0.354*10^{-4} * 4759))}$

$R_L = 0.372$

C 5.3 Freundlich isotherm of monoglyceride

When log(x/m) versus log Ce was plotted, the intercept when Ce = 1.0 is the value of (x/m) and the slope of the line is equal to 1/n .Thus, log(x/m) = -1.2137, and $K_f = 0.06114$ and 1/n = 0.8837 Thus,

$x/m = 0.06114*Ce^{0.8837}$

C 5.4 Langmuir isotherm of monoglyceride

When 1/Ce versus 1/(x/m) was plotted, the interception is 1/a and slope of the line is equal to 1/(ab).

$$\text{When } 1/a = 0.0017$$

$$a = 588.23$$

$$\frac{1}{ab} = 36.34$$

$$b = 0.04678*10^{-3}$$

$$\text{Thus, } x/m = (588.23 * 0.04678*10^{-3}\ Ce)/(1+0.04678*10^{-3}\ Ce)$$

$$R_L = \frac{1}{1+(0.04678*10^{-3}* 8379)}$$

$$R_L = 0.7184$$

The adsorption isotherm of glycerin and glyceride was study and the equation was show as follow:

Freundlish isotherm for glycerin adsorption was

$$\frac{x}{m} = 6.91*10^{-10} *Ce^{3.4601}$$

Langmuir isotherm for glycerin adsorption was

$$\frac{x}{m} = \frac{(-68.4931* 0.354*10^{-4}*Ce)}{(1+(-0.354*10^{-4})*Ce)}$$

Freundlish isotherm for monoglyceride adsorption was

$$\frac{x}{m} = 0.06114*Ce^{0.8837}$$

Langmuir isotherm for monoglyceride adsorption was

$$\frac{x}{m} = \frac{(588.23* 0.04678*10^{-3}*Ce)}{(1+0.04678*10^{-3}*Ce)}$$

C 6 Calculation of treated biodiesel' properties

C 6.1 Calculation of the % free fatty acid (ASTM D5555)

Reagent

1. Ethanol
2. Phenolphthalein
3. 0.25 N NaOH

To the 250 ml of Erlenmeyer flask, oil sample (1 g), ethanol (75 ml) and 2ml of 1% phenolphthalein were added. The mixture was subject to titrate with 0.25 N sodium hydroxide solutions until the pink color was occurred. The ml of alkali solution used was recorded.

The percentage of free fatty acids was calculated as follows:

% free fatty acids = (ml of alkali x N x 28.2) / weight of sample
N = normality of alkaline solution
ml of alkali = ml of sodium hydroxide solution

Table C 9 Values of free fatty acids contain in crude oil

Sample	Weight of sample (g)	Volume of titrant (ml)	Concentration of NaOH (N)	% FFA
Refined palm oil	1.0600	0.10	0.2354	0.62
	1.0679	0.10	0.2354	

C 6.2 Determination of the Saponification value (ASTM D5558)

Reagent

1. Phenolphthalein
2. Alcoholic KOH solution

3. 0.5 N HCl

To the 250 ml of Erlenmeyer flask, oil sample (1 g), alcoholic potassium hydroxide (25 ml) and 1 ml of 1% phenolphthalein were added. The mixture was subject to titrate with 0.5 N of hydrochloric acid until the pink color has disappeared. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was recorded.

The saponification value was calculated as follows:

saponification value = $56.1 \times N \times (A - B)$ / weight of sample
A = titration of blank
B = titration of sample
N = normality of hydrochloric acid solution
Alcoholic KOH = 40 g of potassium hydroxide dissolved in 1 L of ethanol

Table C 10 Saponification value of crude oil

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	SN
Refined palm oil	1.0100	25.45	32.75	201.72[a]
	1.0132	25.50	32.75	

a = 0.4975 N

C 6.3 Determination of the Iodine value (ASTM D5554)

Reagent

1. KOH solution
2. Wijs solution
3. CCl_4
4. 0.1 N $Na_2S_2O_3$
5. Starch

To the 500 ml of Glass-Stopper flask, oil sample (0.1 g), carbon tetra chloride (20 ml) and Wijs solution (25 ml) were added. Store the flasks in a dark place for 30 min. From storage, removed the flasks and add 20 ml of KI solution followed by 100 ml of distilled water. The mixture was subject to titrate with 0.1 N of sodium thiosulfate until the yellow color has almost disappeared, add 2 ml of starch indicator solution, and continued the titration until the blue color has just disappeared. Prepare a blank determination and carried out same with the sample. The ml of sodium thiosulfate used was recorded.

The iodine value was calculated as follows:

Iodine value = $(B - S) \times N \times 12.69$ / weight of sample

B = titration of blank

S = titration of sample

N = normality of $Na_2S_2O_3$ solution

Table C 11 Iodine value of crude oils

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	IV
Refined palm oil	0.1135	41.60	46.90	61.33[a]
	0.1045	42.00	46.90	

a = 0.1035 N

C 6.4 Determination of the acid value (ASTM D974)

Reagent

1. p-naphtholbenzein indicator solution
2. 0.1 M Alcoholic KOH solution
3. Titration solvent (250 ml toluene + 250 ml isopropyl alcohol)

To the 250 ml of Erlenmeyer flask, oil sample (2 g), titration solvent (25 ml) and 0.125 ml of 1% p-naphtholbenzein indicator solution were added. The mixture was subject to titrate with 0.1 M of alcoholic KOH until the green color was occured. Prepare a blank determination and carried out same with the sample. The ml of acid solution used was recorded.

The acid value was calculated as follows:

Acid value = $[(A - B) \times N \times 56.1]$ / weight of sample
A = titration of sample
B = titration of blank
N = normality of alcoholic KOH solution
Alcoholic KOH = 0.6 g of potassium hydroxide dissolved in 100 ml of isopropyl alcohol

Table C 12 Acid value of biodiesels

Sample	Weight of sample (g)	Volume of titrant (ml)	Volume of blank (ml)	AV
1%wt of natural diatomite	2.0016	0.075	0.05	0.0673[a]
	2.0025	0.075	0.05	
Water washing	2.0094	0.075	0.05	0.0671[a]
	2.0053	0.075	0.05	

a = 0.0961 N

C 6.5 Determination of viscosity (ASTM D445)

Viscosity is the unit specifying the resistance to flow; therefore viscosity is normally a specific value.

7 ml of each sample were added into the Viscometer tube, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, Use suction 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. With the sample flowing freely, measure, 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 as follows:

viscosity = Ct

C = Constant of viscometer tube (mm^2/s^2)

time = measured flow times for $t1$ and $t2$, respectively(s)

Table C 13 Viscosity of biodiesels

Sample	Time 1 (s)	Time 2 (s)	Constants of tube	Viscosiy (cSt)
1% wt natural diatomite	289.41	289.77	0.01434[a]	4.15
Water washing	295.78	295.15	0.01434[a]	4.24

VITA

Name: Miss Nisakorn Saengprachum
Date of Birth: June 1, 1985 Birth place: Chainat, Thailand.
Address: 56 Moo 8 Tumbon Chainat, Aumper Muangchainat, Chainat 17000, Thailand, E-mail address: Kuychay511@hotmail.com

Education:

2009	Master of Science in Environmental management Chulalongkorn University, Thailand
2007	Bachelor of Science in Chemistry Chulalongkorn University, Thailand

Conference:

January 21-23, 2010	Pure and Applied Chemistry International Conference 2010 (Paccon 2010), Ubon Ratchathani, Thailand