PRODUCTION OF BIODIESEL THROUGH TRANSESTERIFICATION OF SUNFLOWER OIL USING SiO_2/50%H_2SO_4 SOLID ACIDIC CATALYST

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PRODUCTION OF BIODIESEL THROUGH TRANSESTERIFICATION OF SUNFLOWER OIL USING $SiO_2/50\%H_2SO_4$ SOLID ACIDIC CATALYST

TAN INN SHI

A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

I declare that this thesis entitled “Production of biodiesel through transesterification of sunflower oil using $SiO_2/50\%H_2SO_4$ solid acidic catalyst” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Date : ______________________________

DEDICATION

To my beloved father and mother.

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ABSTRACT

A renewable fuel such as biodiesel, with lesser exhaust emissions, is the need of the day. Hence, researchers and scientific community worldwide have focused on development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially without compromising on the durability of engine parts. Based on the intricacies associated with the homogeneously catalyzed transesterification process, the purpose of the present work is to study biodiesel production by transesterification of sunflower oil with methanol in a heterogeneous system, using silica gel loaded with sulfuric acid ($SiO_2/50\%H_2SO_4$) as a solid acidic catalyst. The catalyst prepared by loading of 50 v/v% H_2SO_4 on silica gel followed by drying it at 110°C. The catalysts were characterized by FTIR, TGA and SEM. The reaction between sunflower oil and methanol is carried out in a 3-necked round bottom flask heated by a rotamantle. The sample is withdrawn at certain time interval and is analyzed using gas chromatography. The dependence of the conversion of sunflower oil on the reaction variables such as the molar ratio of methanol to oil, reaction temperature and catalyst loading was studied. The catalyst has exhibited maximum oil conversion (84wt.%) under the conditions of 100°C, methanol/oil molar ratio of 6:1 and catalyst amount 10%. Kinetic study of reaction was also done. The experimental data is well fitted to the Pseudo-homogeneous model. This optimum operating condition and kinetic model are very important for producing biodiesel fuel effectively in a larger scale.

ABSTRAK

Pada masa kini, bahan bakar yang terbaru seperti biodiesel yang mempunyai pembebasan gas buangan yang lebih rendah diperlukan. Oleh itu, penyelidik and komuniti saintifik dunia telah tertumpu pada pembangunan biodiesel dengan mengoptimumkan proses untuk memenuhi piawaian dan spesifikasi yang diperlukan untuk bahan bakar yang akan digunakan secara komersial tanpa mengganggu jangka hayat sesuatu bahagian mesin. Berdasarkan perkara-perkara yang berkaitan dengan proses pengtransesterifikasi permangkin berhomogen, tujuan kerja ini adalah untuk mempelajari penghasilan biodiesel melalui transesterifikasi minyak bunga matahari dengan methanol di dalam system heterogen dengan menggunakan silika gel yang diisi dengan asid sulfuric ($SiO_2/50\%H_2SO_4$) sebagai pemangkin asid pejal. Pemangkin disediakan dengan menambahkan 50 v/v% H_2SO_4 ke dalam silika gel dan seterusnya dikeringkan pada suhu 110ºC. Ciri-ciri pemangkin telah dianalisa dengan menggunakan FTIR, TGA dan SEM. Tindak balas antara minyak bunga matahari dan methanol telah dilakukan di dalam kelalang bulat berleher-3 yang dipanaskan dengan menggunkan rotamantle. Bahan ujikaji dikeluarkan pada masa tertentu dan dianalisis menggunakan kromatografi gas. Penghubungan antara penukaran minyak bunga matahari terhadap parameter tindak balas telah dipelajari. Pemangkin ini telah menghasilkan penukaran minyak yang maksimum (84 wt%) dibawah keadaan 100ºC dan kadar molar methanol/minyak adalah 6:1 dan loading mangkin 10%. Pelajaran kinetik tindak balas juga telah dibuat. Data eksperimental juga sesuai dengan model Pseudo-homogeneouse. Keadaan operasi yang optimum ini dan model kinetic adalah paling penting dalam penghasilan bahan bakar biodiesel yang effektif di dalam skala yang lebih besar.

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LIST OF ABBREVIATIONS

B100	-	Pure Biodiesl
HSA	-	High Surface Area
FAME	-	Fatty acid methyl esters
GC	-	Gas chromatography
SEM	-	Scanning Electron Microscopy
TGA	-	Thermogravimetric Analyses
FT-IR	-	Fourier Transform Infrared Spectroscopy
SSA	-	Silica sulfuric acid

LIST OF SYMBOLS

$-r_A = -\frac{dC_A}{dt}$	-	The consumption of reactant A per unit time
k’	-	Rate constant
C_A	-	Concentration of A after time t
C_B	-	Concentration of B after time t
	-	Reaction order of reactant A
	-	Reaction order of reactant B
C_{AO}	-	Initial concentration of A
C_{BO}	-	Initial concentration of B
X	-	Conversion
θ_B	-	Ratio of C_{BO} to C_{AO}
A	-	Pre-exponential factor or frequency factor
E	-	Activation energy
R	-	Gas constant
T	-	Absolute temperature

CHAPTER 1

INTRODUCTION

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). The status of present consumption of crude oil is about 79 million barrels per day. The tremendous increasing need of oil, which is predicted to be about 119 million barrels per day by 2020's and the shortage of oil thereafter (after 10-15 years), predicted based on the total reserves in hand, urgently to focus the research in finding alternative means to fulfill world's energy needs. The alternative sources of new and renewable energy such as hydro, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues (Mackenzie, 2008).

Among liquid biofuels, biodiesel derived from vegetable oils is gaining acceptance and market share as Diesel fuel in Europe and the United States. Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources (Hanna, 1999). The development of energy efficient biofuel production technologies in aiming at reducing the reagent costs and increasing the production efficiency is becoming important in a world that is increasingly becoming “green”.

There are more than 350 oil-bearing crops identified, researchers have been led in using different sources of vegetable oil such as peanut, rapeseed, corn, soybean or sunflower seed because there are considered as potential alternative fuels for diesel engines. Table 1.1 shows the oil species that can be used in biodiesel production. Vegetable oil is one of the renewable fuels and potentially inexhaustible sources of energy with an energetic content close to diesel fuel.

Table 1.1: Oil species for biodiesel production (Ayhan, 2009)

Group	**Source of oil**
Major oils	Coconut (copra), corn (maize), cottonseed, canola (a variety of rape seed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower.
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut.
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, baylaurel, beechnut, ben, Borneotallownut, carobpod(algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit(Acrocomia sclerocarpa), meadow foam seed, mustard, okra seed(hibiscus seed), perilla seed, pequi (Caryocar brasiliensis seed), pinenut, poppy seed, prune kernel, quinoa, ramtil(Guizotia abyssinica seed or Niger pea), rice bran, tallow, tea(camellia), thistle(Silybum marianum seed), and wheat germ.
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall.
Other oils	Castor and radish

The vegetable oil fuels were not acceptable because they were more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines (Demirbas, 2003). The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils as diesel fuel are:

- Liquid nature-portability
- Ready availability
- Renewability
- Higher heat content (about 88% of no. 2 diesel fuel)
- Lower sulfur content
- Lower aromatic content
- Biodegradability

The disadvantages of vegetable oils as diesel fuel are:

- Higher viscosity
- Lower volatility
- The reactivity of unsaturated hydrocarbon chains

The major problem associated with the use of pure vegetable oils as fuels, for diesel engines are caused by high fuel viscosity in compression ignition. Diesel boiling range material is of particular interest because it has been shown to significantly reduce particulate emissions relative to petroleum diesel (Giannelos, 2002).

1.1 Biodiesel history

Transesterification of triglycerides are in oils is not a new process. Scientists E. Duffy and J. Patrick conducted it as early as 1853. Life for the diesel engine began in 1893 when the famous German inventor Rudolph Diesel published a paper entitled *‘The theory and construction of a rational heat engine’*. What the paper described was a revolutionary engine in which air would be compressed by a piston to a very high pressure thereby causing a high temperature. Dr. Rudolph Diesel designed the original diesel engine to run on vegetable oil. Dr. Rudolph Diesel used peanut oils to fuel on of this his engines at the Paris Exposition of 1900 (Nitschke, 1965). Because of high temperature created, the engine was able to run a variety of vegetable oils including hemp and peanut oil. At the 1911 World’s Fair in Paris, Dr. Rudolph Diesel ran his engine on peanut oils and declared ‘the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it. One of the first uses of transesterified vegetable oil was powering heavy-duty vehicles in South Africa before World War II. The name ‘biodiesel’ has been given to transesterified vegetable oil to describe its use as a diesel fuel (Demirbas, 2002).

1.2 Properties of biodiesel fuels

Biodiesels are characterized by their viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, carbon residue, copper corrosion, and higher heating value (HHV). The most important parameters affecting the ester yield during the trainsesterification reaction are the molar ratio of alcohol to vegetable oil and reaction temperature. The viscosity values of vegetable oil methyl esters decrease sharply after transesterification. Compared to D2 fuel, all of the vegetable oil methyl esters are slightly viscous. The flash point values of vegetable oil methyl esters are significantly lower than those of vegetable oils. There is high regression between the density and viscosity values of vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are considerably regular. These parameters are all specified through the biodiesel standard, ASTMD 6751. This standard identifies the parameters the pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum-based diesel fuel. Biodiesel, B100, specifications (ASTMD6751–02requirements) are given in Table 1.2.

Table 1.2: Biodiesel, B100, specifications (ASTMD6751–02requirements) (Ayhan. 2009)

Property	**Method**	**Limits**	**Units**
Flash point	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 40 °C	D 445	1.9- 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	wt%
Total sulful	D 5453	0.05 max	wt%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	wt%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerine	D 6584	0.020	wt%
Total glycerine	D 6584	0.240	wt%
Phosphorus	D 4951	0.0010	wt%
Vacuum distillation end point	D 1160	360°C max, at 90°C distilled	°C

1.2.1 Composition of biodiesel

Biodiesel is mixture of fatty acid alkyl esters. If methanol is used as a reactant, it will be a mixture of fatty acid methyl esters (FAME). Based on the feed stock, biodiesel has different proportions of fatty acid methyl esters. Table 1.3 shows the chemical composition of common fatty acids and their methyl esters present in the biodiesel.

Table 1.3: Chemical structures of common fatty acid and their methyl esters

Fatty acid/ Formula/ Molecular weight	**Common acronym**	**Methyl ester/ Formula/ Molecular weight**
Palmitic acid/ $C_{16}H_{32}0_2$/ 256.428	C16:0	Methyl Palmitate/ $C_{17}H_{34}0_2$/ 270.457
Stearic acid/ $C_{18}H_{36}0_2$/ 284.481	C18:0	Methyl Stearate/ $C_{19}H_{38}0_2$/ 298.511
Oleic acid/ $C_{18}H_{34}0_2$/ 282.465	C18:1	Methyl Oleate/ $C_{19}H_{36}0_2$/ 296.495
Linoleic acid/ $C_{18}H_{32}0_2$/ 280.450	C18:2	Methyl Linoleate/ $C_{19}H_{34}0_2$/ 294.479
Linolenic acid/ $C_{18}H_{30}0_2$/ 278.434	C18:3	Methyl Linolenate/ $C_{19}H_{24}0_2$/ 292.463

1.3 The use of vegetable oils and their derivatives as alternative diesel fuels

Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. Due to their high viscosity and low volatility, the direct use of vegetable oils in fuel engines is problematic. The problems are:

(a) Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices.
(b) Carbon deposits
(c) Oil ring sticking
(d) Thickening and gelling of the lubricating oil as result of contamination by the vegetable oils (Hanna, 1999).

Different ways have been considered to reduce the high viscosity of vegetable oils:

(a) Dilution of 25 parts of vegetable oil with 75 parts of diesel fuel,
(b) Microemulsions with short chain alcohols such as ethanol or methanol,
(c) Thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds,
(d) Catalytic cracking, which produces alkanes, cycloakanes and alkybenzenes, and
(e) Transesterification with ethanol or methanol.

Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity, some engine performance problems, such as injector coking and more carbon deposits still exist. At present, the most common way to produce biodiesel is to transesterification of vegetable oil or animal fats with an alcohol in the presence of an alkali or acid catalyst. Among all these alternatives, the transesterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

1.3.1 Composition of oils

Fats and oils are primarily water-insoluble hydrophobic substances of plant and animal origin and are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. Fatty acids vary in carbon chain length and in the number of unsaturated bonds. The fatty acids found in vegetable oils are summarized in Table 1.4. Natural vegetable oils and animal fats are solvent extracted or mechanically pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water. The free fatty acid and water contents have significant effects on the transesterification of glycerides with alcohols using alkaline or acid catalysts. They also interfere with the separation of fatty acid alkyl esters and glycerol because of salt formation in the product.

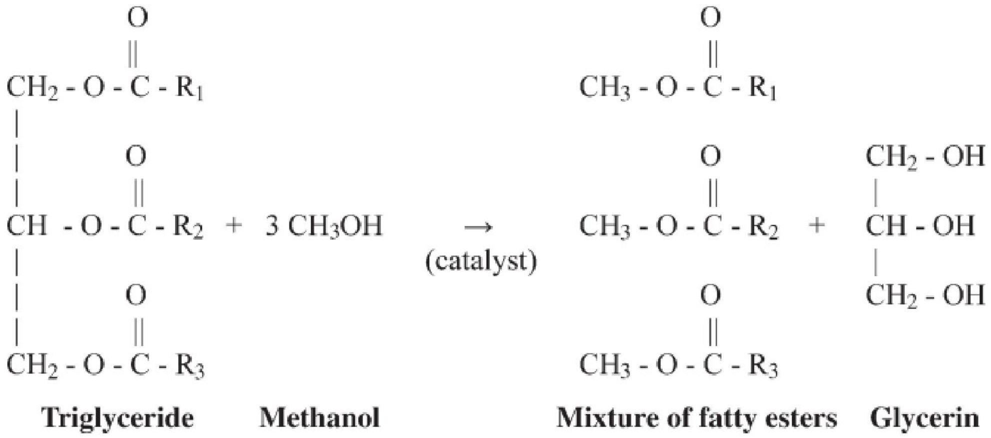
Table 1.4 Fatty acid compositions of vegetable oil samples (Gunstone, 2007)

Vegetable Oil	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**Other**
Sunflower oil	7.0±0.2	3.5±0.1	33.3±0.6	55.2±0.4	0.00	1.0±0.1
Rapeseed	4	2	56	26	10	2
Soybean oil	11	4	33	53	8	2
Palm oil	44	4	40	10	0	2
Values are means± SD of triplicate determinations.						

1.4 Transesterification

The main component of sunflower oil is besides small amounts of stearic acid (1-7%), palmitic acid (4-9%), oleic acid (14-40%) and linoleic acid (48-74%). The demand of renewable combustible derived from vegetable oils increased and has led to the development of oils with methanol and ethanol, involving acidic and base catalysis. More recently, several solid acid catalysts, including H_2SO_4/SiO_2 employed in the organic synthesis are found as efficient and reusable catalysts.

Biodiesel is produced through a process known as transesterification, as shown in the equation below,



Where R1, R2, and R3 are long hydrocarbon chains, sometimes called fatty acid chains. There are only five chains that are most common in soybean oil and animal fats (others are present in small amounts).

Transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin, and creating an alcohol ester. Theoretically, transesterification reaction is an equilibrium reaction. In this reaction, however, more amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product. A catalyst is usually used to improve the reaction rate and yield.

Alcohols are primary or secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently; ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment. However methanol is preferable because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol).

In the conventional transesterification of vegetable oils for biodiesel production, free fatty acids and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst and reduces catalyst effectiveness, all of which resulting in a low conversion (Formo, 1997).

1.4.1 Homogeneous catalysts for transesterification

1.4.1 (a) Alkaline catalysis

Alkaline or basic catalysis is by far the most commonly used reaction type for biodiesel production. The main advantage of this form of catalysis over acid-catalyzed transesterifications is high conversion under mild conditions in comparatively short reaction times (Freedman, 1998). It was estimated that under the same temperature conditions and catalyst concentrations methanolysis might proceed about 4000 times faster in the presence of an alkaline catalyst than in the presence of the same amount of an acidic equivalent (Formo, 1997). Moreover, alkaline catalysts are less corrosive to industrial equipment, and thus enable the use of less expensive carbon-steel reactor material. The main drawback of the technology is the sensitivity of alkaline catalysts to free fatty acids contained in the feedstock material. Therefore alkali-catalyzed transesterifications optimally work with high-quality, low-acidic vegetable oils, which are however more expensive than waste oils. If low-cost materials, such as waste fats with a high amount of free fatty acids, are to be processed by alkaline catalysis, deacidification or preesterification steps are required.

Today most of the commercial biodiesel production plants are utilizing homogeneous, alkaline catalysts. Traditionally the alkoxide anion required for the reaction is produced either by using directly sodium or potassium methoxide or by dissolving sodium or potassium hydroxide in methanol. The advantage of using sodium or potassium methoxide is the fact that no additional water is formed and therefore side reactions like saponification can be avoided. The use of the cheaper catalysts sodium or potassium hydroxide leads to the formation of methanolate and water, which can lead to increased amounts of soaps. However, because of the fact that glycerol separates during alcoholysis reactions, also water is removed out of the equilibrium, so under controlled reaction conditions, saponification can be kept to a minimum.

The amount of alkaline catalyst depends on the quality of the oil, especially on the content of free fatty acids. Under alkaline catalysis free fatty acids are immediately converted into soaps, which can prevent the separation of glycerol and finally can lead to total saponification of all fatty acid material. So the alkaline catalysis is limited to feedstock up to a content of approx. 3 % of fatty acids. There are also other alkaline catalysts like guanidines or anion exchange resins described in literature, however, no commercial application in production plants is known so far. Table 1.5 shows the overview of homogenous alkaline catalysts.

Table 1.5: Overview of homogenous alkaline catalysts (Mustafa, 2010).

Type of Catalyst	**Comments**
Sodium hydroxide	Cheap, disposal of residual salts necessary
Potassium hydroxide	Reuse as fertilizer possible, fast reaction rate, better separation of glycerol
Sodium methoxide	No dissolution of catalyst necessary, disposal of salts necessary.
Potassium methoxide	No dissolution of catalyst necessary, use as fertilizer possible, better separation of glycerol, higher price.

1.4.1 (b) Acid catalysis

Acid catalysis offers the advantage of also esterifying free fatty acids contained in the fats and oils and is therefore especially suited for the transesterification of highly acidic fatty materials. However, acid-catalyzed transesterifications are usually far slower than alkali-catalyzed reactions and require higher temperatures and pressures as well as higher amounts of alcohol. The typical reaction conditions for homogeneous acid-catalyzed methanolysis are temperatures of up to 100°C and pressures of up to 5 bars in order keep the alcohol liquid (Lepper, 1998). A further disadvantage of acid catalysis – probably prompted by the higher reaction temperatures – is an increased formation of unwanted secondary products, such as dialkylethers or glycerol ethers (Mittelbach, 1996).

Because of the slow reaction rates and high temperatures needed for transesterification, acid catalysts are only used for esterification reactions. Thus for vegetable oils or animal fats with an amount of free fatty acids larger than approx. 3 % two strategies are possible. The free fatty acids can either be removed by alkaline treatment, or they can be esterified under acidic conditions prior to the alkaline catalyzed transesterification reaction. This so-called pre-esterification has the advantage that prior to the transesterification most of the free fatty acids are already converted into FAME, thus the overall yield is very high. If the free fatty acids are simply removed prior to the transesterification (similar to the deacidification of vegetable oils during refining) on the one side the transesterification conditions do not have to be changed, however, on the other hand, these fatty acids are lost in the overall yield unless these fatty acid are esterified in a separate step.

The cheapest and best known catalyst for esterification reactions is concentrated sulphuric acid. The main disadvantage of this catalyst is the possibility of the formation of side products like dark colored oxidized or other decomposition products. The organic compound p-toluene sulphonic acid can also be used; however the high price of the compound so far prevented broader application. As heterogeneous catalyst also cationic ion exchange resins can be used in continuous reaction columns, however, this approach has only be used so far in pilot plants. Table 1.6 shows the overview of acidic catalysts.

Table 1.6: Overview of acidic catalysts (Mustafa, 2010).

Type of Catalyst	**Comments**
Conc. sulphuric acid	Cheap, decomposition products, corrosion.
p-Toulene-sulphonic acid	High price, recycling necessary.
Acidic ion exchange resins	High price continues reaction possible, low stability.

1.4.2 Heterogeneous catalysts for transesterification

Although traditional homogeneous catalysis offers a series of advantages, its major disadvantage is the fact that homogenous catalysts cannot be reused. Moreover, catalyst residues have to be removed from the ester product, usually necessitating several washing steps, which increases production costs. Thus there have been various attempts at simplifying product purification by applying heterogeneous catalysts, which can be recovered by decantation or filtration or are alternatively used in a fixed-bed catalyst arrangement. The most frequently cited heterogeneous alkaline catalysts are alkali metal- and alkaline earth metal carbonates and oxides (refer Table 1.7). For the production of biofuels in tropical countries, Graille et al. (1998) recommended utilizing the ashes of oil crop waste (e.g. coconut fibers, shells and husks) (Graille,1998). The resulting natural catalysts are rich in carbonates and potassium oxide and have shown considerable activity in transesterifications of coconut oil with methanol and water free ethanol.

Among the catalysts listed in Table 1.7, the application of calcium carbonate may seem particularly promising, as it is a readily available, low-cost substance. Moreover, the catalyst showed no decrease in activity even after several weeks of utilization (Suppes, 2001). However, the high reaction temperatures and pressures and the high alcohol volumes required in this technology are likely to prevent its commercial application. The reaction conditions described sometimes are so drastic, that there might be also conversion without any use of catalyst. Mostly, comparison experiments without any catalyst are missing in the experiments.

Table 1.7: Overview on heterogeneous catalyst.

Catalyst type	**Examples**	**References**
Alkali metal carbonates and hydrogen carbonates	Na_2CO_3, $NaHCO_3$, K_3CO_3, $KHCO_3$	(Dae, 2009)
Alkali metal oxides	K_2O (produced by burning oil crop waste)	(Zhu, 2006)
Alkali metal salts of carboxylic acids	Cs-laurate	(Dae, 2009)
Alkaline earth metal alcoholates	Mixtures of alkali/alkaline earth metal oxides and alcoholates.	(Meher, 2006)
Alkaline earth metal carbonates	$CaCO_3$	(Suppes, 2001)
Alkaline earth metal oxides	CaO, SrO, BaO	(Xuejun, 2008)
Alkaline earth metal hydroxides	$Ba(OH)_2$	(Nalan, 2007)
Alkaline earth metal salts of carboxylic acids	Amberlyst A 26, A 27	(Michikazu, 2009)
Metal phosphates	Ortho-phosphates of aluminum, gallium or iron(III)	(Di, 2007)
Transition metal oxides, hydroxides and carbonates	$Fe_2O_3(Al_2O_3)$, Fe_2O_3, Fe_3O_4, FeOOH, NiO, Ni_2O_3, $NiCO_3$, $Ni(OH)_2Al_2O_3$	(Santacesaria, 2006)
Transition metal salts of amino acids	Zn- and Cd-arginate	(Meher, 2006)
Transition metals salts of fatty acids	Zn- and Mn-palmitates and stearates	(Meher, 2006)
Silicates and layered day minerals	Na-/ k-silicates, Zn-, Ti- or Sn-silicates and aluminates	(Dae, 2009)
Zeolite catalysts	Titanium-based zeolites, faujasites	(Maria, 2008)

Similar drawbacks have to be attested for alkali metal or alkaline earth metal salts of carboxylic acids. The use of strong alkaline ion-exchange resins, on the other hand, is limited by their low stability at temperatures higher than 40°C and by the fact that free fatty acids in the feedstock neutralize the catalysts even in low concentrations. Finally, glycerol released during the transesterification process has a strong affinity to polymeric resin material, which can result in complete impermeability of the catalysts (Bondioli, 2004). Most recently, the first technology using heterogeneous catalysts like zinc oxides or zinc aluminates, has been used in a commercial biodiesel production plant in France. The so-called Esterfip-H process was developed by the Institut Français du Pétrole (IFP) and was designed and commercialized by Axens. The main advantages of the process are described as the production of high quality glycerol and no need for disposal of salts resulting from the catalyst. However, the overall economic advantages have to be proved in long term operation (Stern, 2000).

1.5 Identification of problems

A renewable fuel such as biodiesel, with lesser exhaust emissions, is the need of the day. Hence, researchers and scientific community worldwide have focused on development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially without compromising on the durability of engine parts. The interest in the use of renewable fuel started with the direct use of vegetable oils as a substitute for diesel. However, their direct use in compression ignition engines was restricted due to high viscosity which resulted in poor fuel atomization, incomplete combustion and carbon deposition on the injector and the valve seats causing serious engine fouling. Conventionally homogeneous catalysts (like NaOH, KOH etc.) are used for the transesterification reaction. Since the transesterification reaction can only occur in the interfacial region between the liquids (Benitez, 2004) and also fats and alcohols are not totally miscible (Stavarache, 2005), this is a very slow process. Despite industrial applicability, homogeneous catalysts have their own limitations, especially those associated with homogeneously catalyzed processes. The catalyst dissolves fully in the glycerin layer and partially in the FAME layer. As a result, biodiesel should be cleaned through a slow, tedious and an environmentally unfriendly water washing process. Catalyst contaminated glycerin has little value in today's market and is increasingly becoming a disposal issue. Another negative aspect of the homogeneously catalyzed process is that the catalysts are not re-usable. Heterogeneous catalysts, on the other hand, make product separation easier and make catalysts reusable. With the use of solid catalysts, the refining steps in the purification process can be reduced. Also, heterogeneous catalysts have the potential to simplify the production process by enabling usage of continuous packed bed reactors.

1.6 Objectives of the study

Based on the intricacies associated with the homogeneously catalyzed transesterification process, the overall goal of this study is to design and develop a heterogeneously catalyzed chemical process to produce biodiesel in an efficient manner.

The objectives of the project are:

1. To study the feasibility of producing biodiesel using heterogeneous catalysis ($SiO_2/50\%H_2SO_4$).
2. To identify the important variables for the transesterification process.
3. To develop the kinetic model for the transesterification process.

1.7 Scope of the study

In the present study, several important parameters have been investigated. These parameters are ratio of alcohol to oil, temperature, and amount of catalyst used. The detail of the scope is as below:

1. Temperature is between 60°C-100°C.
2. Amount of catalyst is between 5g-12g.
3. Ration of alcohol to oil is 6:1 to 12:1.

1.9 Rationale and Significance

Rationale. The objective of the present studies is to perform the transesterification of sunflower oil for the production of biodiesel using heterogeneous catalysis and assisted by heating.

Significance. The majority of the biodiesel production around the world is carried out by employing the homogeneous base catalyzed process because it is kinetically much faster than heterogeneously catalyzed transesterification and is economically viable. However, because of separation problems and product quality concerns, extensive research on heterogeneous catalysis towards the biodiesel production is ongoing all over the world.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development.

1. It provides a market for excess production of vegetable oils and animal fats.
2. It decreases, although will not eliminate, the country’s dependence on imported petroleum.
3. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel (Sheehan, 1998).
4. The exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower than with regular diesel fuel.
5. When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel.

CHAPTER 2

REVIEW OF LITERATURE

2.1 Introduction

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial (Krawczyk, 1996)

While biodiesel is generally more expensive to produce than petroleum diesel, it also emits significantly less pollution. Subsidies are required for adoption of biodiesel outside of niche markets.

2.2 Solid catalysis in biodiesel production

The majority of the biodiesel production around the world is carried out by employing the homogeneous base catalyzed process because it is kinetically much faster than heterogeneously catalyzed transesterification and is economically viable. However, because of separation problems and product quality concerns, extensive research on heterogeneous catalysis towards the biodiesel production is ongoing all over the world.

In general the factors which govern the path of transesterification reactions are nature of raw materials, types of catalysts and optimum experimental conditions (temperature, oil to methanol ratio and catalyst concentration). As far as experimental condition is concerned for the generation of methyl ester with high yield, optimization of certain parameters or the application of optimized parameters are necessary. For example, a solid base catalyst, prepared under the specified conditions of 3.5 wt% KNO_3 loadings on Al_2O_3 substrate followed by calcinations at 773 K for 5 h produced the catalytic group of Al-O-K and favored the conversion of soybean oil in to methyl esters (Xie, 2006) with a FAME yield of more than 75%. Similarly, a heterogeneous base catalyst, Na/NaOH/γ-Al_2O_3, employed under the optimized reaction conditions such as the reaction time, the stirring speed, and oil to methanol ratio explored the catalytic activity equal to homogeneous NaOH catalyst. The conversion rate was increased over two orders of magnitude to the homogeneous reaction with several of the zeolite catalysts when metals are considered as catalysts (Suppes, 2004). They recommended temperatures of 25-65°C and a catalyst concentration of 1-3% for optimum transesterification yields. Moreover they also observed the largest conversions taking place in sodium hydroxide and zirconium based catalysts and the use of immobilized lipase catalyst failed to produce methyl esters.

Demirbas (2003) revealed that the commonly accepted molar ratios of alcohol to glycerides for the transesterification of vegetable oils are 6:1-30:1. The change in catalyst-to-oil ratio under the reaction conditions of temperature of 650°C, residence time 2.6 s and steam-to-oil weight ratio of 0.83 was explored. It was found that there was a slight increase in biodiesel production efficiency at the beginning stage and then, a decrease in biodiesel yield slightly thereafter which could be attributed to cracking of FAME at that higher temperature. The common reason for the change in the value of the catalyst-to-oil weight ratio is the change in contact conditions between oil and catalysts which in turn changes the average activation of catalysts. In general, as the catalyst-to-oil weight ratio increases, the probability of contact between oil and active centers also increases. Under these conditions, maximum transfer of energy is possible favoring easier transesterification.

Even though the role of homogeneous catalysts are significant for the industrial or large scale production of biodiesel and for easy conversion at moderate temperatures (40 to 65°C), some of the major disadvantages in using such catalysts during transesterification are its soluble tendency into the reaction mixtures which prevents the separation process. It has been reported that (Certinkaya, 2004), the solubility of homogeneous catalysts either in biodiesel layer and or in glycerin layer is possible to a certain extent. Current methods such as bubble washing, spray washing, counter current washing, and agitation are extensively used to wash and purify the contaminated products. However, these processes are considered time consuming and uneconomical. Besides, catalysts contaminated crude glycerol which is separated by gravitational settling or centrifuging and is valued low in present markets which compounds the seriousness of the separation issue.

Another problem associated with transesterification is the presence of water in the reaction mixture which causes the soap formation via saponification. An interesting remedial measure suggested (Filip, 1992) in relation of minimizing or preventing the soap formation is the use of 2 or 3 mol% K_2CO_3. The key role of K_2CO_3 in this case is the formation of corresponding bicarbonate salt instead of water. Similarly during the production of non digestible polyol polyesters through interesterification of fatty acids with polyols, e.g. sucrose, several improvements, such as the application of low temperature and/or high pressure for increasing the mass transfer area, using back mixing in the initial stages, and plug-flow conditions in the final stages have been exercised.

As compared to homogenously catalyzed process, the transesterification with solid catalyst occurs at harsher reaction conditions i.e. at higher temperatures and pressures. This is because of the fact that the solid catalyzed process is an immiscible liquid/liquid/solid 3-phase system (corresponding to oil, methanol & catalyst) (Singh, 2007) that is highly mass transfer limited. In one study, supported solid catalysts CaO/MgO was used (Wang, 2005) for the transesterification of rapeseed oil at a relatively low temperature of 65°C by impregnating on a MgO support followed by calcination at 700°C in Ca(Ac)2 solution. The catalyst showed higher activity with a glycerol yield of more than 80% purity. In other work (Serio, 2006) soybean oil was transesterified at 100°C with methanol using MgO and calcined hydrotalcites (CHT) as catalysts. Four different basic sites were individuated at MgO and the calcined hydrotalcites for the transesterification and the strongest basic site was able to do the transesterification reaction below 100°C. More than 45% of biodiesel yield was observed in case of MgO and more than 75% yield was observed in case of CHT. It was reported that at a higher temperature of 200°C, more than 95% of yield was observed for MgO and CHT catalysts. Biodiesel production with High Surface Area (HSA) nanocrystalline metal oxides on TiO_2 , MgO and CaO supports were investigated (Dean, 2006). M-Acetylacetonate (AcAc) was supported on the HSA support where M being Na, K, Ca, Li, V, Fe, N, and Al. The best catalysts tested were CaO and AcAc supported on MgO and TiO_2.

In a different work biodiesel production of jatropha curcas (Zhu, 2006) oil with a solid catalyst CaO dipped in ammonium nitrate followed by calcination at 900°C showed an oil conversion of 93% at 70°C after 3.5 hrs of transesterification. The catalyst dosages and the oil to methanol ratio used in the study were 1.5 % and 9:1 respectively. In other work of soybean oil transesterification (Liu, 2007) with SrO as a heterogeneous catalyst, a yield in excess of 90% was observed below 70°C within 30 min. A long catalyst lifetime of SrO was also investigated as it sustained the activity after repeated used for 10 cycles.

2.3 Effect of different parameters on production of biodiesel

2.3.1 Effect of reaction temperature

The conversion rate increases with reaction time. Freedman et al. (1984) transesterified peanut, cotton-seed, sunflower and soybean oil under the condition of methanol-oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93-98%). Ma et. At (1999) studies the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeds very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min.

Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied with three different temperatures (Freedman, 1984). After 0.1 h, ester yields were 94%, 87% and 64% for 60°C, 45°C and 32°C, respectively. After 1 h, ester formation was identical for 60°C and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters (Hanna, 1999).

2.3.2 Effect of methanol to oil ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to oil. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters (Tomasevic, 2003). However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters. The transesterification of Cynara oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield increased as the molar ratio increased up to a value of 12:1. The best results were for molar rations between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the separation of glycerol remains in the biodiesel phase. Therefore, molar ratio 9:1 seems to be the most appropriate (Enciner, 2002).

The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mss transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters (Zhou, 2003). The emulsions are caused in part by formation of the intermediates monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains. These intermediates are strong-surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, the concentration of mono- and di-glycerides are very low, then the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of mono- and di-glycerides.

Since methanol to oil ratio has a significant impact on the FAME production and glycerol produce depending the oil and catalyst used, this effect will be further investigated in this study.

2.3.3 Effect of catalyst loading

Yang and Xie (2007) studied the effect of catalyst loading on the conversion of soybean oil in the range of 1.0-9.0 % with reference to the starting oil weight. This studied using strontium metal-doped ZnO as the catalyst. They found that when the amount of catalyst was increased from 1.0-4.0%, the conversion to methyl esters showed a gradual increase. The maximum value of 94.7% of biodiesel yield was achieved at 5 % of catalyst loading. Xie and Li (2006) reported that the transesterification reaction was strongly dependent upon the catalyst used. Without the addition of a catalyst, transesterification did not occur, while the presence of the supported catalyst significantly increased the reaction rate. High conversion of biodiesel was obtained at 2.5 % of catalyst loading. This studied used potassium loaded on alumina as a solid-base catalyst.

Results by Liu et al. (2007b) indicate that with more catalyst addition, reaction rate become faster and reached equilibrium at 4.0% of catalyst amount because of the increase in the total number of available active catalytic sites for the reaction. Xie et al. (2007) varied the catalyst amount in the range of between 1.0-6.0% with reference to the starting oil weight. Kim et al. (2004) revealed that with increasing catalyst loading, the slurry (mixture of catalyst and reactants) became more viscous. This gave rise to a problem of mixing and a demand of higher power consumption for adequate stirring. This studied used metal oxides as the catalyst. From the reported literature, the optimum catalyst loading is defined as the loading that will give high FAME yield and does not contribute to the mixing problem in the reaction mixture at the same time. Thus, the optimum loading will be further investigated in this study as well.

2.4 Kinetics of transesterification

2.4.1 Early Kinetic Studies

Although the importance of biodiesel as an alternative fuel has grown in the last twenty years, the chemical kinetics of transesterification, the most common means of producing biodiesel, remain controversial. Most efforts in the literature have focused on finding the best fit of empirical data to simple models of reaction order. Some of these results are contradictory. The one paper that develops a kinetic model based on chemical mechanisms has never been referenced. (Komers 2002)

Work on chemical kinetics specific to biodiesel production began with Freedman and colleagues at USDA in the early 1980's (Freedman 1984, 1986). It was found that the forward reactions appear to be pseudo-first order or second order depending upon conditions used. Reverse reactions appeared to be second order. At MeOH/Oil molar ratio of 6:1, a shunt reaction was observed. Activation energies were determined for all forward and reverse reactions under a variety of experimental conditions for plots for log k vs. 1/T (where k is the rate constant and T is the temperature).

In 1990, Mittelbach and Trathnigg of Karl Franzen University, Austria, discussed the kinetics of methanolysis of sunflower oil. Although they did not propose any rate equations or derive any rate constants, they did discuss the parameters affecting the transesterification reaction. Mittelbach found that the conversion of triglycerides did not follow second-order kinetics as indicated by Freedman. He found that the rate of reaction is temperature dependent, but the percent conversion is not a strong function of temperature provided that the reaction proceeds at least ten minutes (Mittelbach 1990).

In the past, it has been observed that the base catalyzed transesterification is a second order reaction (Darnoko, 2000). This has been confirmed in a different work for the transesterification of soybean oil with methanol using sodium hydroxide a homogeneous catalyst (Noureddini, 1997). In this work, it was assumed that transesterification is a three-step reversible process, and the reaction rate constants and activation energies were determined for all the forward and reverse reactions. The transesterification of soybean oil with methanol or 1-buthanol proceeded according to pseudo first-order or second-order kinetics, depending on the molar ratio of alcohol to soybean oil, whereas the reverse reaction was second order.

2.4.2 Latest work

The acid-catalyzed processes and the corresponding kinetic studies included the use of sulfuric acid as a catalyst ([Sendzikiene et al., 2004], [Berrios et al., 2007] and [Santacesaria et al., 2007]), whereas in the study of Santacesaria et al. (2007), a sulfonic active group-functionalized copolymer matrix gel was applied as a catalyst as well. Once again, all the studies employed conventional oils, such soybean oil (Santacesaria et al., 2007), sunflower oil (Berrios et al., 2007), and rapeseed oil (Sendzikiene et al., 2004). It must be pointed out, however, that major drawbacks – such as reactor corrosion and the substantial generation of by products and waste materials, including the salts formed as a result of the mineral acid neutralization, which must be disposed of in the environment – represent insurmountable problems for the mineral-acid-catalyzed process.

The kinetics of biodiesel production can usually be differentiated by the mechanism of the transesterification process. Three novel processes and the corresponding kinetic studies include the use of tin chloride as a catalyst (Cardoso et al., 2009), the use of lipase as a biocatalyst ([Al-Zuhair, 2005], [Al-Zuhair et al., 2007] and [Cheirsilp et al., 2008]), and the use of non-catalytic supercritical alcohol ([Dasari et al., 2003], [Minami and Saka, 2006] and [He et al., 2007]). Regardless of the process, however, all the studies employed conventional oils, such as soybean oil ([Al-Zuhair, 2005], [Dasari et al., 2003] and [He et al., 2007]), sunflower oil (Berrios et al., 2007), palm oil ([Al-Zuhair et al., 2007] and [Cheirsilp et al., 2008]), and rapeseed oil (Minami and Saka, 2006). Nevertheless, most of today’s biodiesel comes from the transesterification of edible resources, such as animal fats, vegetable oils, and even waste cooking oils, in conditions of acid and alkaline catalysis.

In most industrial biodiesel processes, however, the starting oil is added to methoxide (methanol and an alkali metal base) and mixed for some time at a temperature just below the boiling point of methanol, followed by settling and washing. This stage represents the most investigated area of research in the field of base-catalyzed biodiesel production kinetics ([Noureddini and Zhu, 1997], [Bambase et al., 2007], [Slinn and Kendall, 2009], [Cao et al., 2009], [Darnoko and Cheryan, 2000], [Karmee et al., 2004], [Dorado et al., 2004], [Vicente et al., 2006], [Karmee et al., 2006], [Lee et al., 2007] and [Stamenkovic et al., 2008]). These base-catalyzed processes and the corresponding kinetic studies include the use of either sodium ([Noureddini and Zhu, 1997], [Bambase et al., 2007], [Slinn and Kendall, 2009] and [Cao et al., 2009]) or potassium ([Darnoko and Cheryan, 2000], [Karmee et al., 2004], [Dorado et al., 2004], [Vicente et al., 2006], [Karmee et al., 2006], [Lee et al., 2007] and [Stamenkovic et al., 2008]) hydroxide as a catalyst, although in the study of Karmee et al. (2004), tetrahydrofuran was also applied as a co-solvent. All the studies employed oils such as soybean oil ([Noureddini and Zhu, 1997] and [Lee et al., 2007]), sunflower oil ([Bambase et al., 2007] and [Stamenkovic et al., 2008]), palm oil (Darnoko and Cheryan, 2000), rapeseed oil (Cao et al., 2009), Pongamia pinnata oil ([Karmee et al., 2004] and [Karmee et al., 2006]), olive oil (Dorado et al., 2004), and Brassica carinata oil (Vicente et al., 2006). On the other hand, in more than a few of the mentioned studies of the base-catalyzed process the reaction kinetics are simplified ([Slinn and Kendall, 2009], [Darnoko and Cheryan, 2000], [Dorado et al., 2004], [Lee et al., 2007] and [Stamenkovic et al., 2008]). A survey on the mechanism and kinetics reaction is given in Table 2.1.

Table 2.1: A survey on the mechanism and kinetics reaction.

No.	**Oil**	**Alcohol**	**Catalyst**	**T, °C**	**Reaction mechanism**	**Kinetics model**	**Reference**
1.	Sunflower oil	Methanol	KOH	25-65	Three consecutive reversible reactions	Second-order	Vicente et al. (2005)
2.	Brassica carinata oil	Methanol	KOH	25-65	Three consecutive reversible reactions	Second-order	Vicente et al. (2006)
3.	Sunflower oil	Methanol	KOH	30	Three consecutive reversible reactions	Second-order	Stamenkovic et al. (2007)
4.	Palm oil	Methanol	Sodium hydroxide	60-100	Three consecutive reversible reactions	Second-order	Narvaez et al. (2007)
5.	Soybean oil	Methanol	KOH	70-100	Three consecutive reversible reactions	Pseudo-first-order	Lee et al.(2007)

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter discusses the materials, equipments and methods used in this study. Table 3.1 shows the functions of each component in the experiment setup

3.2 Materials & Equipments

The following chemicals will be employed for the transesterification process:

1. Sunflower oil
2. Methanol
3. Catalyst (silica gel, and aqueous H_2SO_4)

Table 3.1: The functions of each component in the experiment setup.

No.	**Apparatus/ Equipments**	**Function**
1.	Three neck round bottom flask	As reactor for the reaction mixture.
2.	Heating mantle	To supply heat to the reactor.
3.	Thermocouple	To measure the temperature inside the reactor.
5.	Condenser	To condense the distillate.
6.	Magnetic stirrer	To stir the reaction mixture.
7.	Beaker	To hold and pour liquids.
8.	Oven	To dry the catalyst.
9.	Desiccator	To cool the catalyst to room temperature.
10.	Gas chromatography	To analysis the raw materials and sample.
11.	Scanning Electron Microscopy (SEM)	To study solid surfaces and the properties of catalysts.
12.	Thermogravimetric Analyses (TGA)	To measure the thermal stability of the catalyst.
13.	Fourier Transform Infrared Spectroscopy (FTIR)	To verify the presence of H_2SO_4 on the silica gel.

3.3 Experimental

3.3.1 Catalysts Preparation

The supported catalysts SiO_2/50% H_2SO_4 was prepared through the following procedures:

10.0g of silica gel and 100mL of aqueous H_2SO_4(50%) were mixed in a beaker and the suspension stirred at room temperature for 30 min. the resulting solid was filtered and dried at 110ºC for 12 h in an oven and cooled to room temperature in a desiccators.

3.3.2 Catalyst Characterization

3.3.2.1 Thermogravimetric Analyses (TGA)

Thermogravimetric analyses were performed for the acidic silica gel with a TGA Q500 V6.4 Build 193 apparatus (heating rate 10ºC min^{-1}) using synthetic air (AGA, > 99.99%) as a reactive gas and nitrogen (AGA, >99.99%) as a protective gas. A sample of the test material is placed into a high alumina cup that is supported on, or suspended from an analytical balance located outside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

3.3.2.2 Fourier Transform Spectrometers (FT-IR)

A Thermo Nicolet Avatar 370 DTGS instrument was used to verify the presence of H_2SO_4 on the silica gel. A background spectrum is first obtained by collecting an interferogram (raw data), followed by processing the data by Fourier transform conversion. This is a response curve of the spectrometer and takes account of the combined performance of source, interferometer, and detector. The background spectrum also includes the contribution from any ambient water (two irregular groups of lines at about 3600 cm^{-1} and about 1600 cm^{-1}) and carbon dioxide (doublet at 2360 cm^{-1} and sharp spike at 667 cm^{-1}) present in the optical bench. Next, a single-beam sample spectrum is collected. It contains absorption bands from the sample and the background (air).

3.3.2.3 Scanning Electron Microscopy (SEM)

An Evo 50 Zei SS instrument was used to study solid surfaces and the properties of catalysts. The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

3.3.3 Activity studies

The batch transesterification reaction system employed in this work is shown in Fig. 3.1-3.2. A 250 mL three necks round bottom flask equipped with magnetic stirrer, thermometer and condenser was used in all experiment. The reactor was immersed in constant temperature heating mental which was capable of controlling the temperature to within deviation of 5ºC.

The procedure that was used for each reaction is as follows; the reactor was initially charged with sunflower oil depending upon the require molar ratio of oil to Methanol and the corresponding amount of SiO_2/50% H_2SO_2 catalyst was added. The reactor assembly was then placed in constant heating mantle and heated to the desired temperature. The reaction was timed as soon as magnetic stirrer turned on. Experiment was carried out by changing different parameters like temperature, methanol/oil molar ratio, and reaction time and catalyst amount. Approximately 8-9 samples were collected during the course of each reaction. Samples were collected in 2 mL vials. The samples were analyzed for its composition by using gas chromatography (GC).

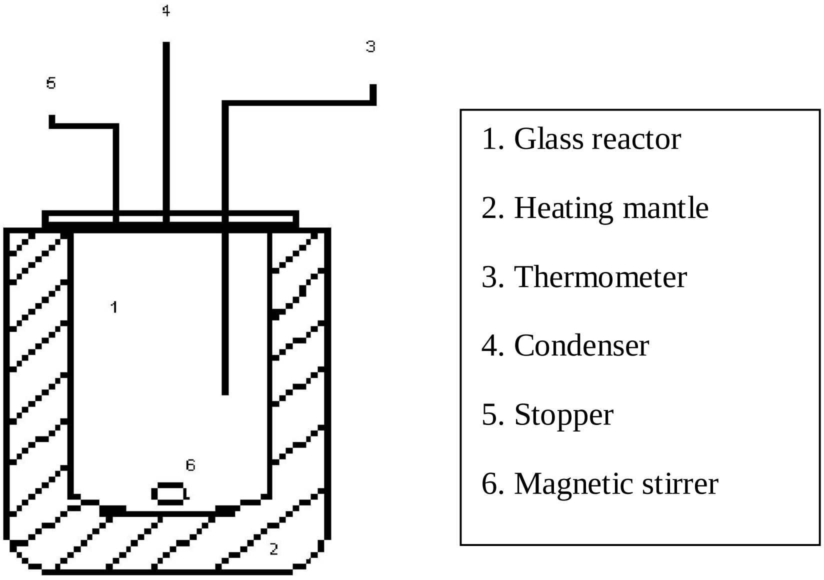


Figure 3.2: The schematic diagram of batch transesterification system.

3.3.4 Gas Chromatography Analysis

Samples obtained from the top layers of the mixture were sent for GC analysis. A GC equipped with an Hp-Wax capillary column (30m×0.25mm×0.25µm) uses to analysis the raw materials and sample. The oven was first held at 50°C for 1 min, and then ramped to 180°C at a rate of 15°C/min for 11.67 min. Finally the oven was ramp to 230°C at a rate of 7°C/min for 23.81 min.

3.3.4.1 Standards preparation

Table 3.2 and 3.3 outline the concentrations of the working and stock standards that were used in the analysis. There are normally two internal standards, one for the higher volatile components and the other for the lower volatile components. Tricaprin was used as the only internal standard to correct for internal disturbances in the analysis.

Table 3.2: Concentration of stock standards

Component	**mg/mL**	**Volumetric Flask (mL)**	**Mass of the sample (mg)**
Methyl Palmitate	25	10	250
Methyl Oleate	25	50	1250
Methyl Linoleate	25	50	1250
Tricaprin	2	10	20
Butanol	2	10	20

Table 3.3: Concentration of working Standards

Component — &	**S1**	**S2**	**S3**	**S4**	**S5**
Methyl Palmitate	500	1000	1500	2000	2500
Stock	0.2	0.4	0.6	0.8	1.0
Methyl Oleate	500	1000	1500	2000	2500
Stock	0.2	0.4	0.6	0.8	1.0
Methyl Linoleate	500	1000	1500	2000	2500
Stock	0.2	0.4	0.6	0.8	1.0
Tricaprin	100	100	100	100	100
Stock	0.5	0.5	0.5	0.5	0.5
Butanol	100	100	100	100	100
Stock	0.5	0.5	0.5	0.5	0.5

3.3.4.1(a) Procedure for stock standards preparation

The stock standard was weighed out the appropriate amount of standard required in a volumetric flask e.g. 250 mg methyl palmitate in a 10 mL volumetric flask for a concentration of 25 mg/mL, then make up the flask with n-Heptane to the 10 mL mark.

3.3.4.1(b) Procedure for working standards preparation

The working standard was pipetted into a volumetric flask with an appropriate volume of each stock solution of methyl palmitate, methyl oleate, methyl linoleate and tricaprin to the 10mL volumetric flask and then dilutes to mark with n-Heptane, cap and mix.

3.3.4.2 Samples preparation

Weight out 50-70mg of sample into a 10mL volumetric flask and mass recorded. Add 250 L of Tricaprin IS and dilute to the mark with n-Heptane, cap and mix.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst characterization

Recently, silica sulfuric acid (SSA) has been widely used as a reusable, heterogeneous, inexpensive solid Brønsted acid catalyst and has received much attention (Pore, 2006) and there has been increasingly awareness about the use of solid acids such as silica sulfuric acid (SSA) for transesterification (Masoud, 2009). SSA is a strong Brønsted and Lewis acid, presumably arising from the formation of − sites on the surface. This heterogeneous catalyst can be easily separated from the reaction media, has greater selectivity, and is recyclable, easier to handle, more stable, nontoxic, and insoluble in organic solvents. The goal of this work was to characterize the sulfuric acid supported on silica gel by Thermogravimetric Analyses, Fourier Transform Spectrometers (FT-IR) and Scanning Electron Microscopy (SEM).

4.1.1 Thermogravimetric analyses (TGA)

This analysis was done in order to determine the weight profile of silica sulfuric acid (SSA) at different temperatures. Figure 4.1-4.2 shows the TGA curve for the catalyst before and after use in the experiments. The total weight lost with different temperature regions for the catalyst before and after use in the experiments are illustrated in Figure 4.3-4.4. The weight losses found from TGA measurements agree fairly well with those expected for the decomposition of silica sulfuric acid to silica and .

For the catalysts of both cases, the thermo gravimetric curves seems to indicate two-stage decomposition which considered to be due to removal of physical absorbed water $(80° - 110°)$, or basic silica sulfuric acid (120°C-330°C), respectively, and is involved with a total overall weight loss of catalyst 51% for the catalyst before use and 28% for the catalyst after use. The total overall weight loss of the catalyst that being use was less than the catalyst that before use, this is because the water in the catalyst lost during the reaction. Therefore, weight loss seems to be lesser for the catalyst after use.

During the thermo gravimetric analysis of silica gel there is a continual loss of water over a temperature range from 30^{o}C about 1050^{o}C. Water can be held on the surface of the silica gel by different interaction forces; by 'dispersive forces' (*e.g.* physically bound water), 'polar forces' (*e.g.* hydrogen bonded water), or, by 'chemical forces' (*e.g.* silanol groups that condense to siloxane bonds with the release of water). As a result of the interaction forces between the adsorbed water and the silica surface, each molecule has a potential energy of adsorption. Furthermore, the silanol groups must acquire sufficient kinetic energy before they can condense to siloxane bonds and generate water. As the temperature is raised, so the kinetic energy of the adsorbed water and silanol groups increases and when the energy is equivalent or greater than the potential energy of adsorption or chemical combination, water will leave the surface in vapor form. Due to the number of different ways that water can be held on the surface of the silica gel, there will be a number of different sources of desorbable water.

These different sources might be considered as groups of adsorbed or combined water, within which, the potential energies of adsorption for each water molecule will be similar but not necessarily identical to one another. Conversely, between groups, the mean potential energy of the adsorbed or combined water may be widely different, as the temperature range over which all the water is evolved, is large. The distribution of adsorption energy within a group could take one of many forms.

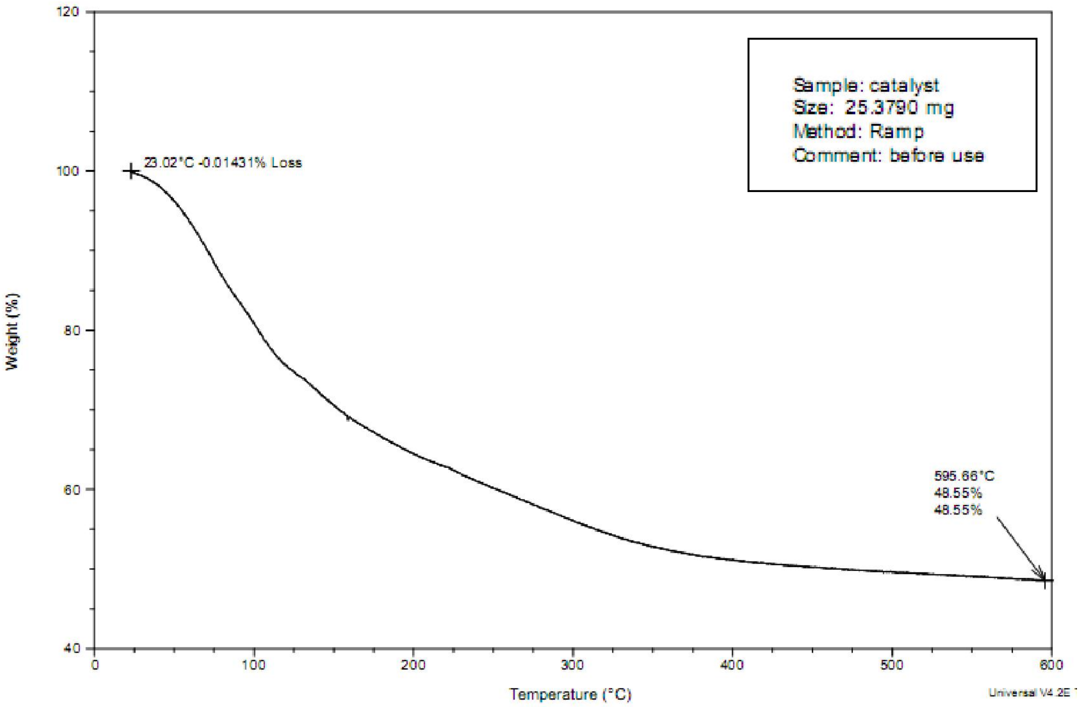


Figure 4.1: Percent weight change against the reference material temperature. (Before use)

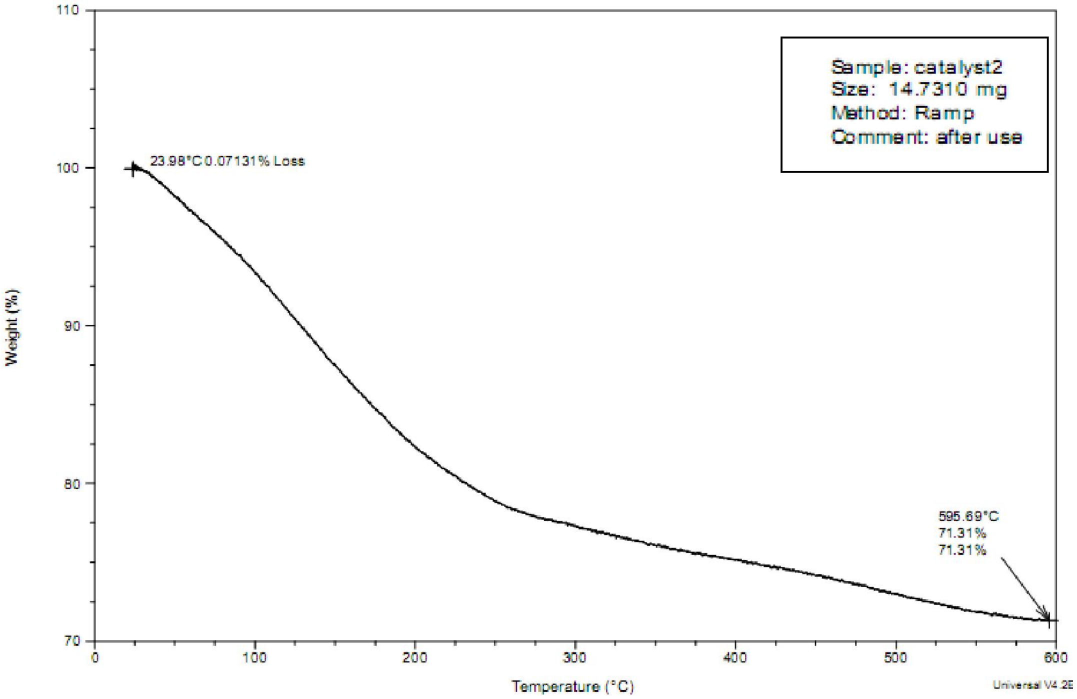


Figure 4.2: Percent weight change against the reference material temperature. (After use)

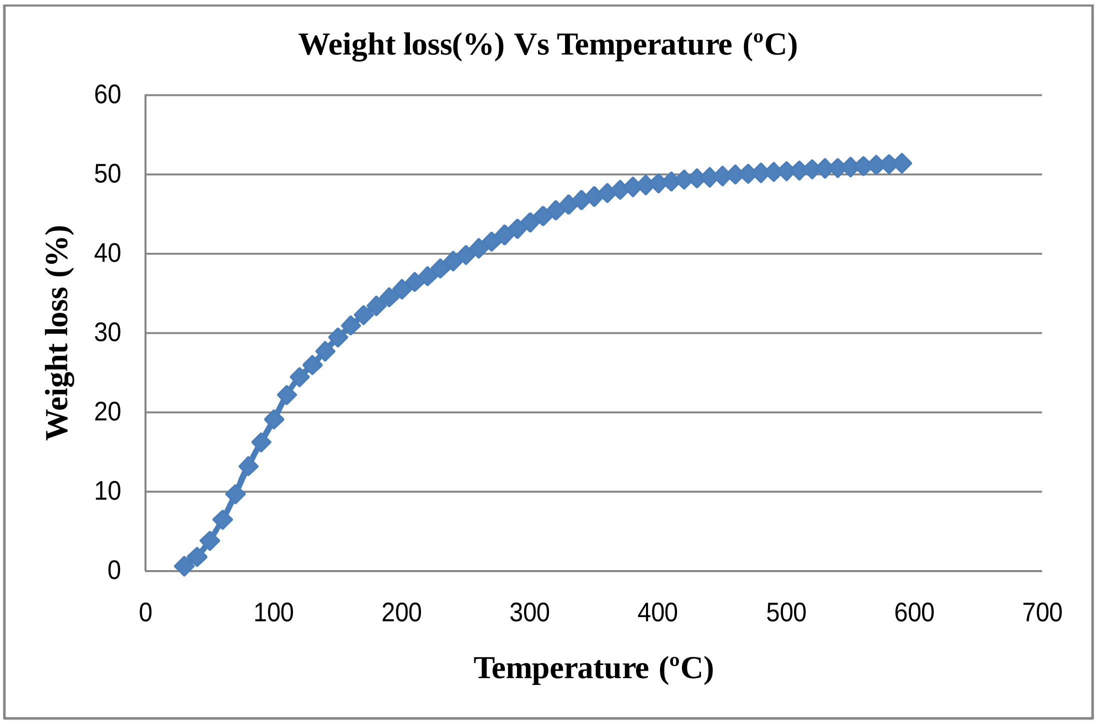


Figure 4.3: Weight loss curve for silica sulfuric acid. (Before use)

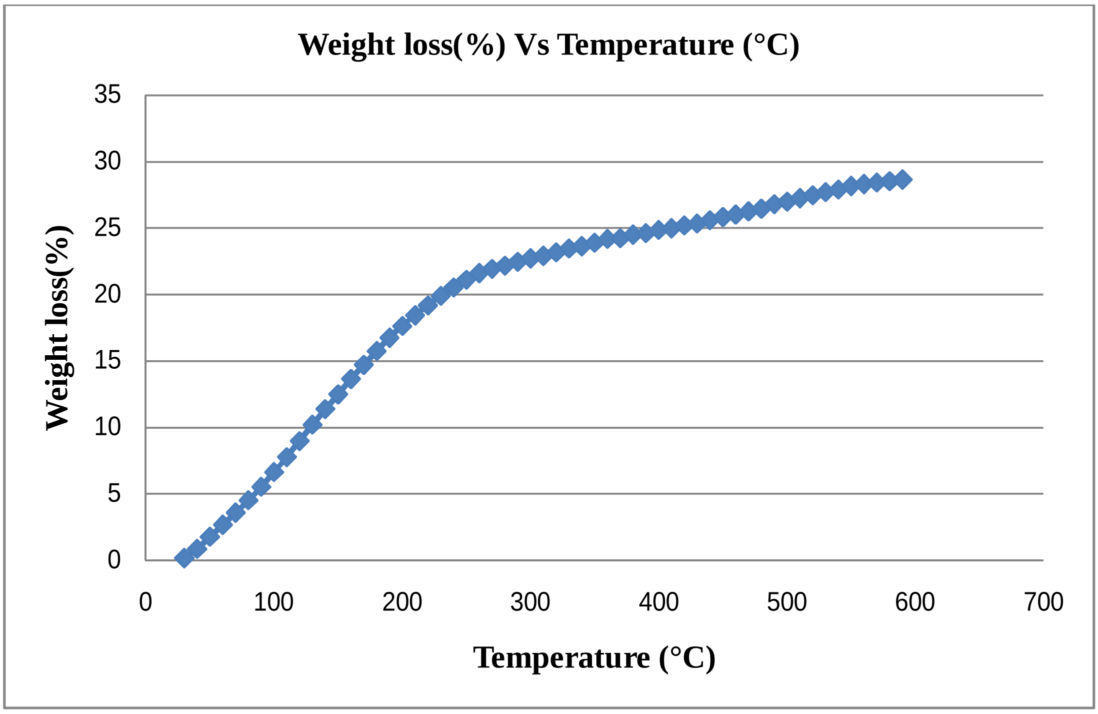


Figure 4.4: Weight loss curve for silica sulfuric acid. (After use)

4.1.2 FT-IR of silica sulfuric acid

The FT-IR spectrum of the silica was shown in Figure 4.5 and the FT-IR spectrum of the catalyst was shown in Figure4.6 (a)-4.6 (b). For the silica (SiO_2), the major peaks are broad anti symmetric Si-O-Si stretching from 403cm^{-1}-490cm^{-1} and symmetric Si-O-Si stretching near 565cm^{-1}(Gnanakumar, 2008). For sulfonic acid functional group, the FT-IR absorption range of O=S=O asymmetric and symmetric stretching modes lies in around 1024cm−1 and1080cm−1 (Jaafar, 2007) and 880-1010 cm^{-1}respectively and that of the S-O stretching mode lies in 570-600 cm^{-1}.

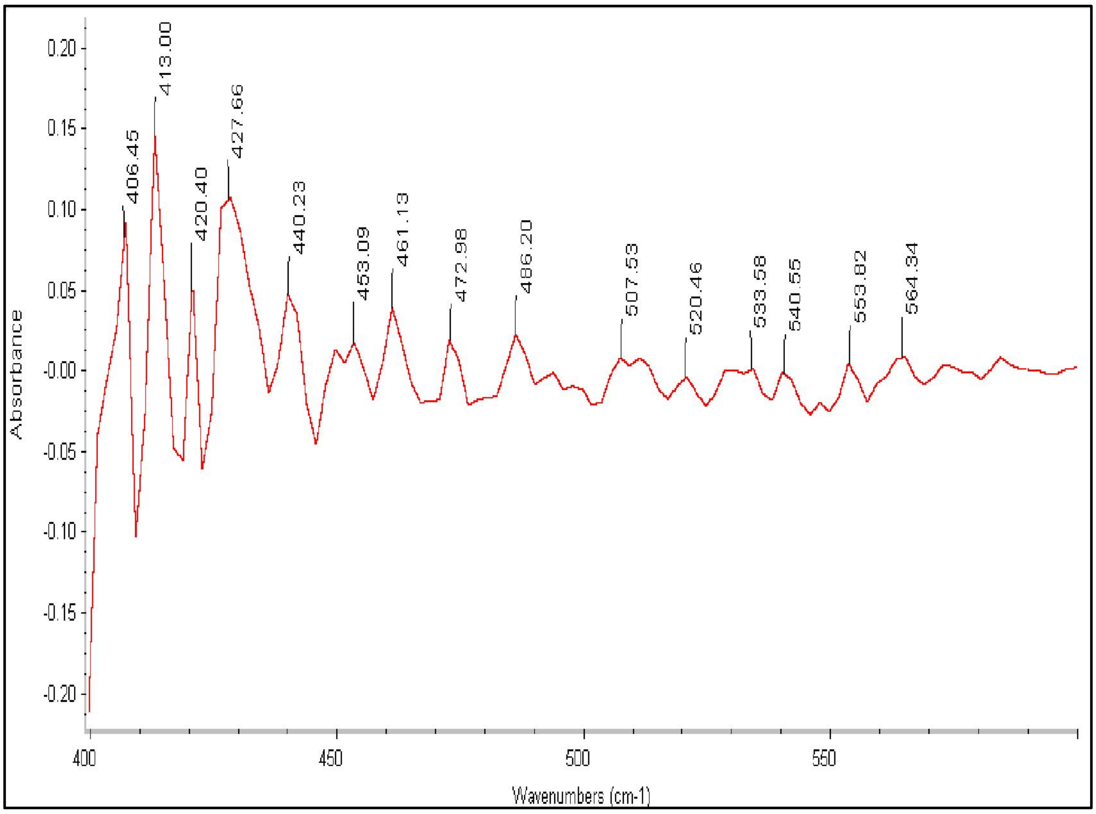


Figure 4.5: FT-IR spectra of silica.

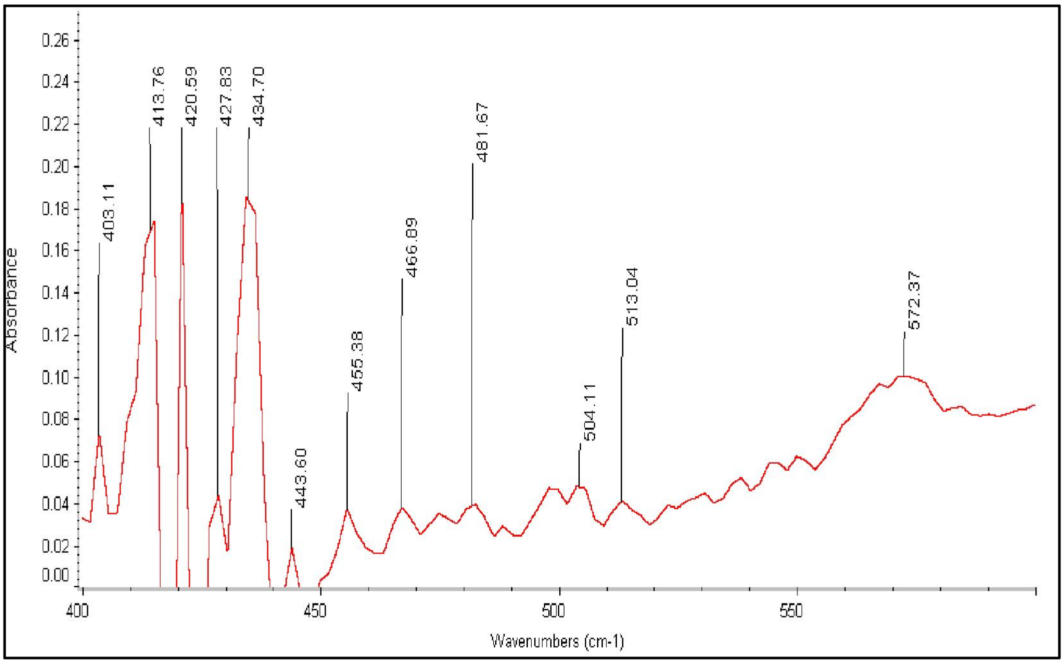


Figure 4.6(a): FT-IR spectra of silica sulfuric acid. (Wave numbers 400cm^{-1}**-600**cm^{-1})

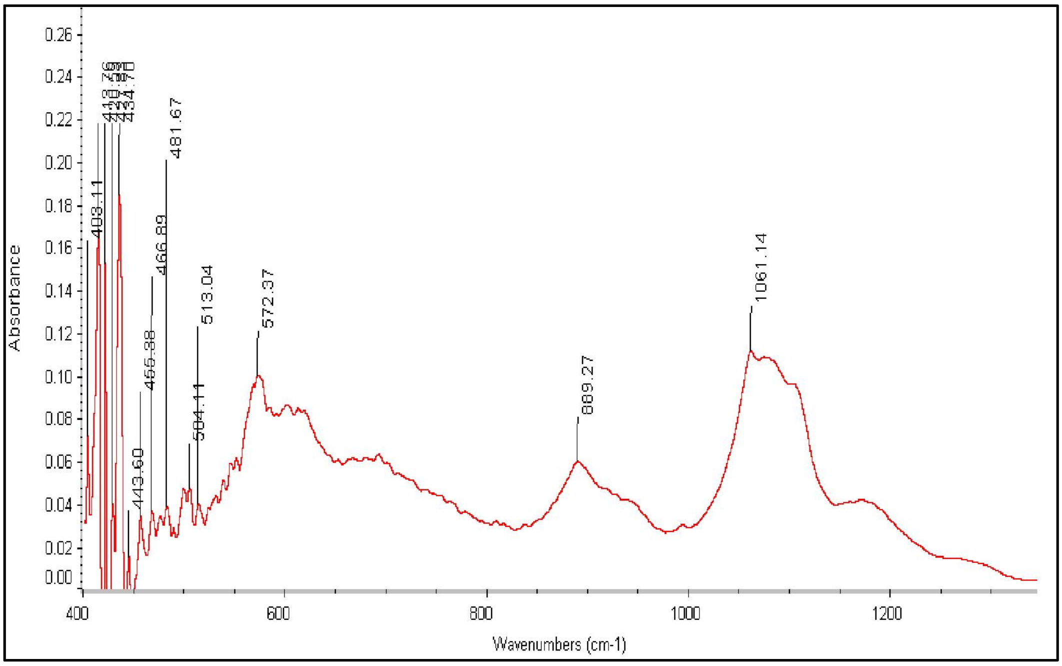


Figure 4.6(b): FT-IR spectra of silica sulfuric acid. (Wave numbers 400cm^{-1}**-1300**cm^{-1})

4.1.3 Scanning electron microscopy (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. Figure 4.7-4.8 shows the SEM image for silica sulfuric acid at different magnifications. The sample dried in the drying oven shows a higher surface roughness (porosity). This can be explained by higher evaporation rate that take place on the surface compared to the bulk of particles, causing shrinkage of the aggregate. The crystal form in SEM images shown the presence of sulfuric acid on the silica gel.

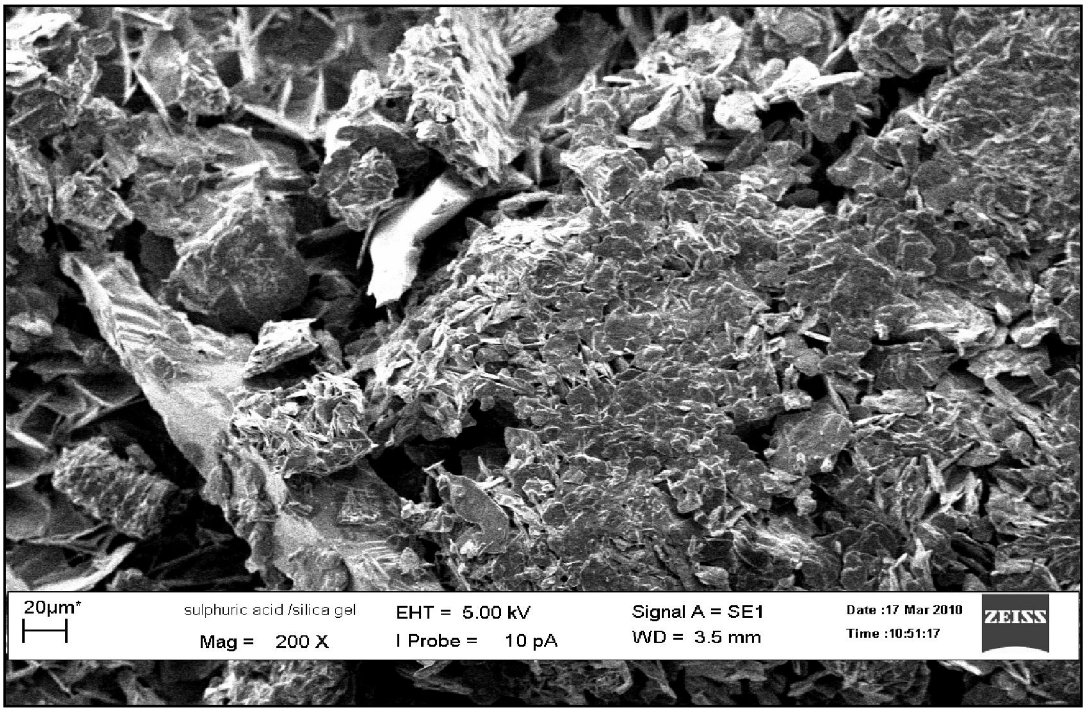


Figure 4.7: SEM image of silica sulfuric acid (200X).

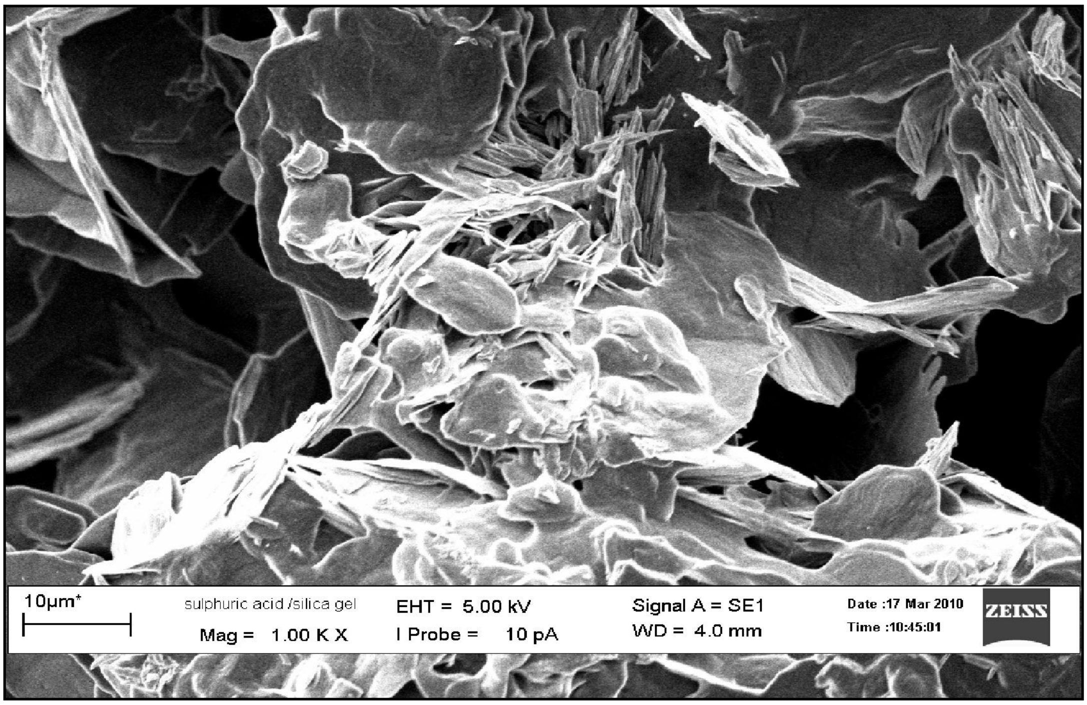


Figure 4.8: SEM image of silica sulfuric acid (1000X)

4.2 Gas Chromatography (GC) analysis

By using GC three different methyl esters were identified according to their retention time which was based on their molecular weight (Table 4.1). Three identified methyl esters were methyl palmitate, methyl oleate and methyl linoleate. There were some other small peak present in the gas chromatogram but these were ignored as insignificant. For the convenience of quantification only these three methyl esters concentrations were determined and compared. Before testing any of the biodiesel samples a repeat (x2) injection of the same methyl esters standard solution was run to test precision. Then a five point calibration series of three methyl esters mixed standard solution was also run to test the reliability of the GC performance and accuracy. The GC chromatograms are shown in Appendix A. Microsoft Excel was used to draw a calibration and generate the calibration equation.

Table 4.1: Retention time for methyl esters.

Methyl esters	**Retention time(min)**
Methyl palmitate	16.375
Methyl oleate	16.820
Methyl linoleate	17.792

4.2.1 Calibration curves of the methyl esters

Three calibration curves were plotted for the three methyl esters. They were found to be linear over the range 500-2500 µg/mL. The calibration curves are shown in Figures 4.9-4.11 and the data used to plot the curves is given in Tables 4.2-4.4.

4.2.1(a) Methyl palmitate calibration equation

Table 4.2 Methyl palmitate peak area series data

Concentration µg/mL	**Peak area**
500	84.8747
1000	227.967
1500	326.745
2000	366.662
2500	435.198

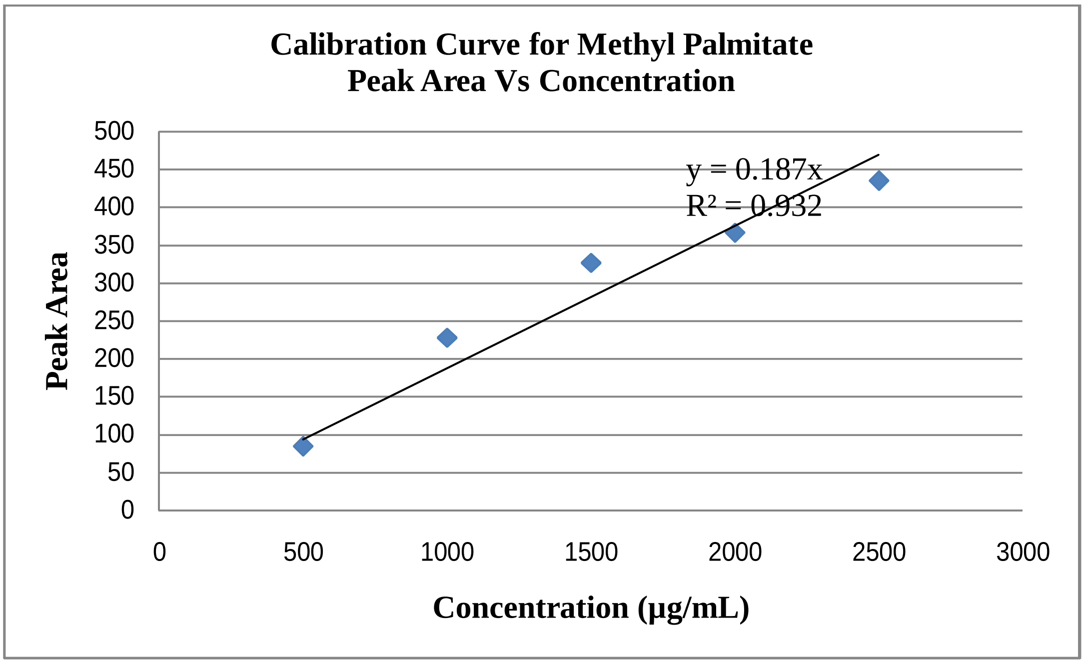


Figure 4.9: Methyl palmitate calibration curve and equation.

4.2.1 (b) Methyl oleate calibration equation

Table 4.3 Methyl oleate peak area series data

Concentration µg/mL	**Peak area**
500	65.0801
1000	85.0801
1500	155.741
2000	249.423
2500	312.77

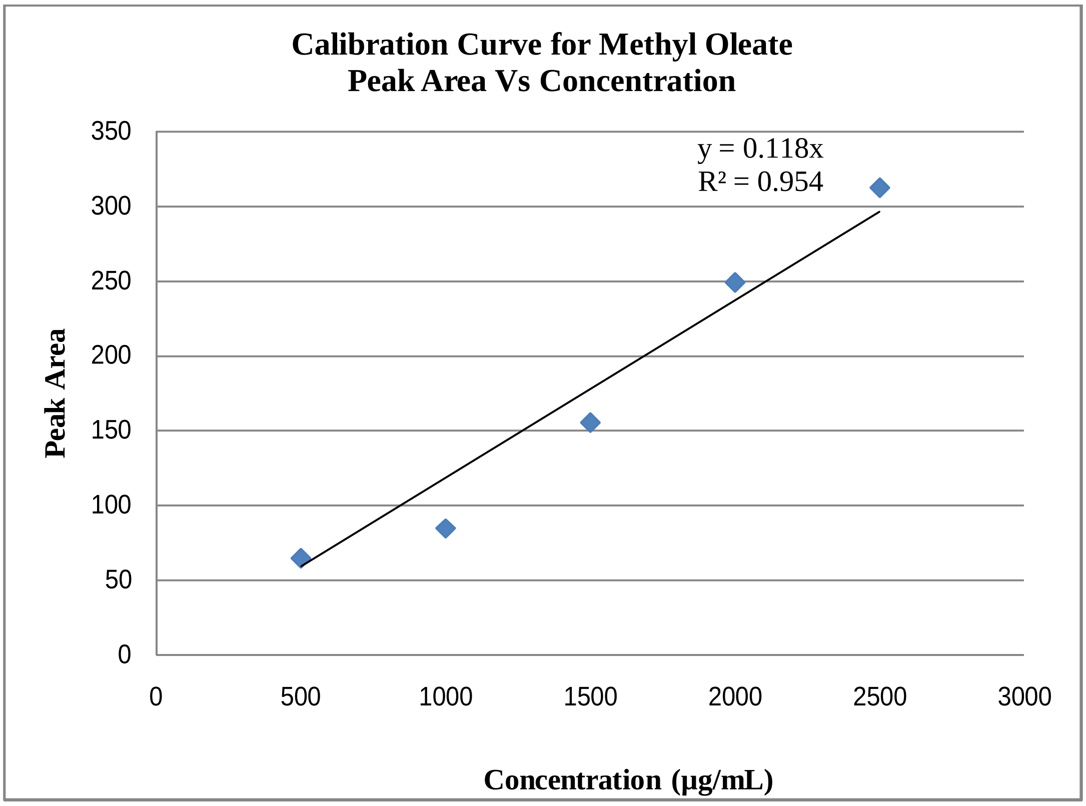


Figure 4.10: Methyl oleate calibration curve and equation.

4.2.1 (c) Methyl linoleate calibration equation

Table 4.4 Methyl linoleate peak area series data

Concentration µg/mL	**Peak area**
500	36.9865
1000	63.5535
1500	85.9335
2000	122.712
2500	153.568

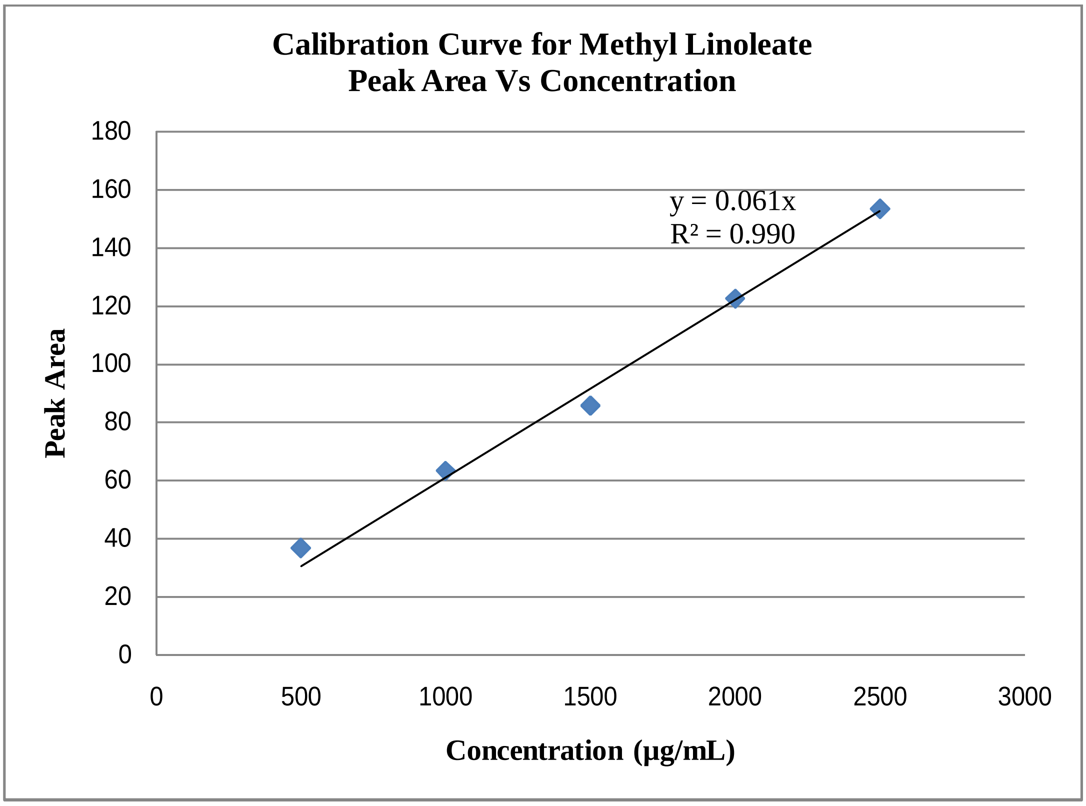


Figure 4.11: Methyl linoleate calibration curve and equation.

4.3 Catalytic activity experimental studies

In order to speed up the formation of methyl esters, various parameters such as temperature, amount of catalyst and molar ratio of methanol to oil were varied and the best operating condition for methyl esters production were determined along based on the composition of finally obtained methyl esters obtained. The typical analysis calculation is shown in Appendix B.

4.3.1 Effect of temperature

During the study of the effect of temperature on reaction duration, the molar ratio of methanol to oil was fixed at 6:1 and the catalyst amount at 10%. As illustrated in Figure 4.12, the conversion increase with the increases in temperature. The reaction was studied at three different temperatures. After 3.33 hr, oil conversions were 29.76%, 38.97% and 84.83% for 60, 70 and 100ºC, respectively. The temperature influenced the reaction rate and % oil conversion significantly. Increasing the temperature of a reaction increases the kinetic energy of the particles which increases the number of collisions so the reaction rate increases. Increasing the kinetic energy of reactant particles also means more of the reactant particles will have the minimum amount of energy required to form products (i.e., activation energy) which leads to more successful collisions and therefore increases the reaction rate.

Further increase in temperature is reported to have a negative effect on the conversion (Barnwal, 2005). If oil is exposed to higher temperature (>200ºC), the degradation of triglycerides and unsaturated fatty acids leads to the formation of undesirable polymeric products (Kulkarni, 2006). Moreover, due to limitations of experimental set up, the reactions were not conduction above 130ºC. Thus, SiO_2/50% H_2SO_4 catalyst has exhibited the highest conversion of sunflower oil of the magnitude 84.83% at 100ºC under given set of reaction conditions.

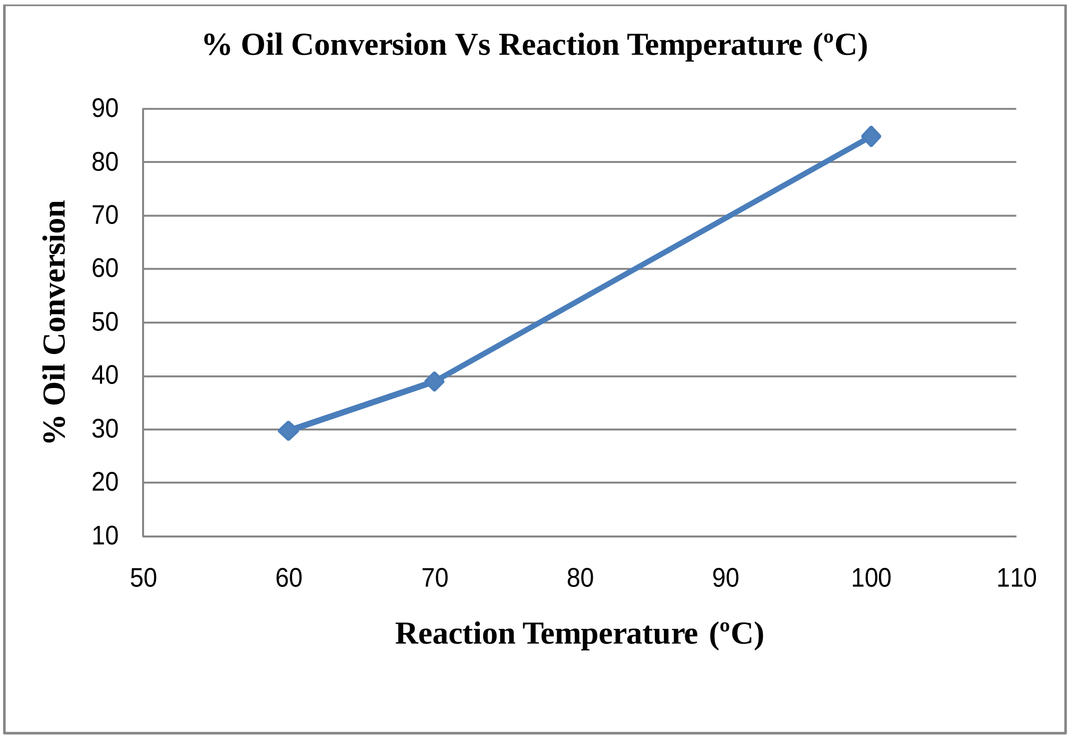


Figure 4.12: Influence of reaction temperature on the conversion. Reaction conditions: molar ratio of methanol to oil=6:1, catalyst amount=10% (wt/wt), and reaction time=3.33hr.

4.3.2 Effect of catalyst amount

The effect of the amount of SiO_2/50% H_2SO_4 catalyst on the oil conversion was investigated. The catalyst amount was varied in the range of 10-24% (wt/wt) and keeping all other reaction parameters identical. Each reaction was carried out at 70ºC for 4.33 hr using molar ratio of methanol to oil of 6:1. Based on these results, the activity profile was established and illustrated in Figure 4.13. The highest conversion of 48.78% was obtained at catalyst loading of 10% (wt/wt). It can clearly seen from Figure 4.13 that, when the amount of SiO_2/50% H_2SO_4 catalyst was increased from 10% to 24%, conversion was found to decrease, which was possibly a mixing effect involving reactants, products and solid catalyst. Probably, above 10% catalyst loading, higher viscosity of reaction mixture might be responsible for the poor diffusion between the methanol-oil-catalyst systems (Kotwal, 2009). Thus, it is clear that increase in catalyst above 10% (wt/wt) did not help to improve the conversion.

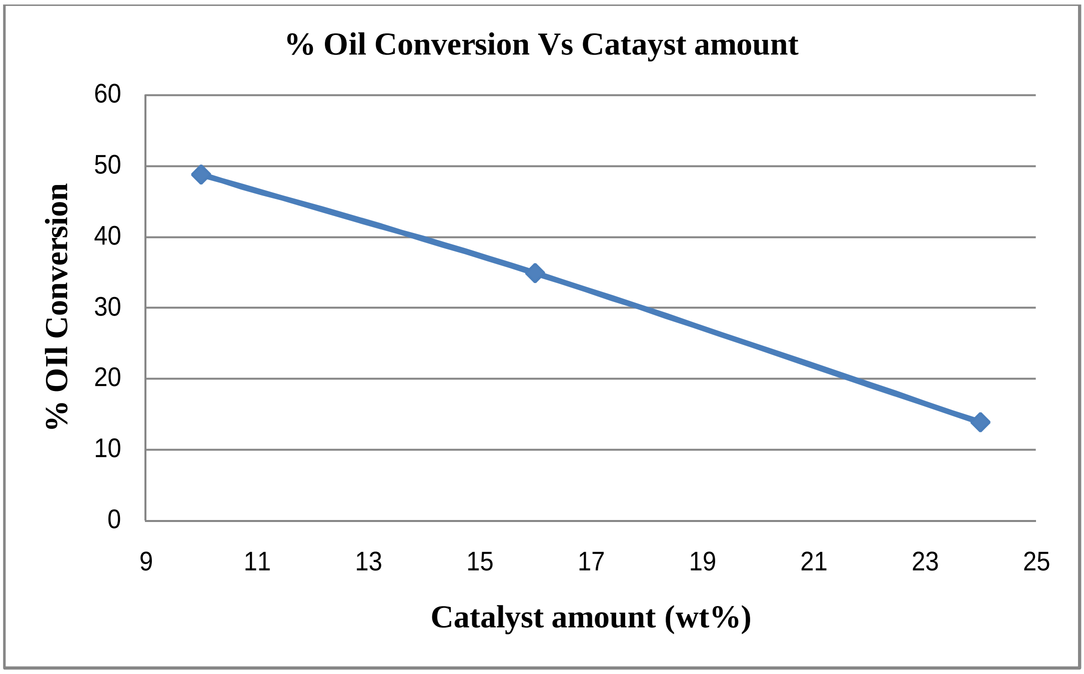


Figure 4.13: Influence of catalyst amount on the conversion. Reaction conditions: Sunflower oil 50g, reaction time 4.33hr, molar ratio of methanol to oil: 6:1, and reaction temperature 70ºC.

4.3.3 Effect of molar ratio of alcohol to oil

One of the most important parameters affecting the conversion of oil is the molar ratio of alcohol to vegetable oil. In the present work, the molar ratio of methanol to oil was varied in the range of 6:1 to 12:1 and its influence on the conversion was investigated. Figure 4.14 shows the effect of methanol to oil molar ratio on the conversion at the end of 5.33 hr reaction time at 70ºC in the present of 10% of SiO_2/50% H_2SO_4 catalyst. When the ratio was increased from 6:1 to 12:1, the conversion was found to decrease from 68.60% to 21.50%. The highest conversion of 68.60% was registered at molar ratio of 6:1. Theoretically, the transesterification of oil requires three moles of methanol per mole of triglyceride. Since transesterification of triglyceride is a reversible reaction, the excess of methanol shifts the equilibrium towards the direction of ester formation. Nevertheless, further increase in the methanol amount has not show any significant improvement in the conversion. On the contrary, use of molar ratio of 12:1 resulted in drop in conversion. Probably, higher concentration of methanol interferes with the separation of glycerin because of its increased solubility. It is also possible that presence of glycerin in the solution might drive equilibrium to backward direction yielding lower contribution of glycerin in the product or may cause etherification of glycerol in presence of larger amount of methanol. Moreover, it was observed that for high molar ratio a longer time require for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as emulsifier that enhances emulsion. Therefore, increasing the molar ratio of methanol/oil beyond 6:1 did not increase the conversion, but complicated the ester recovery process and raised the cost for methanol recovery (Leung, 2006).

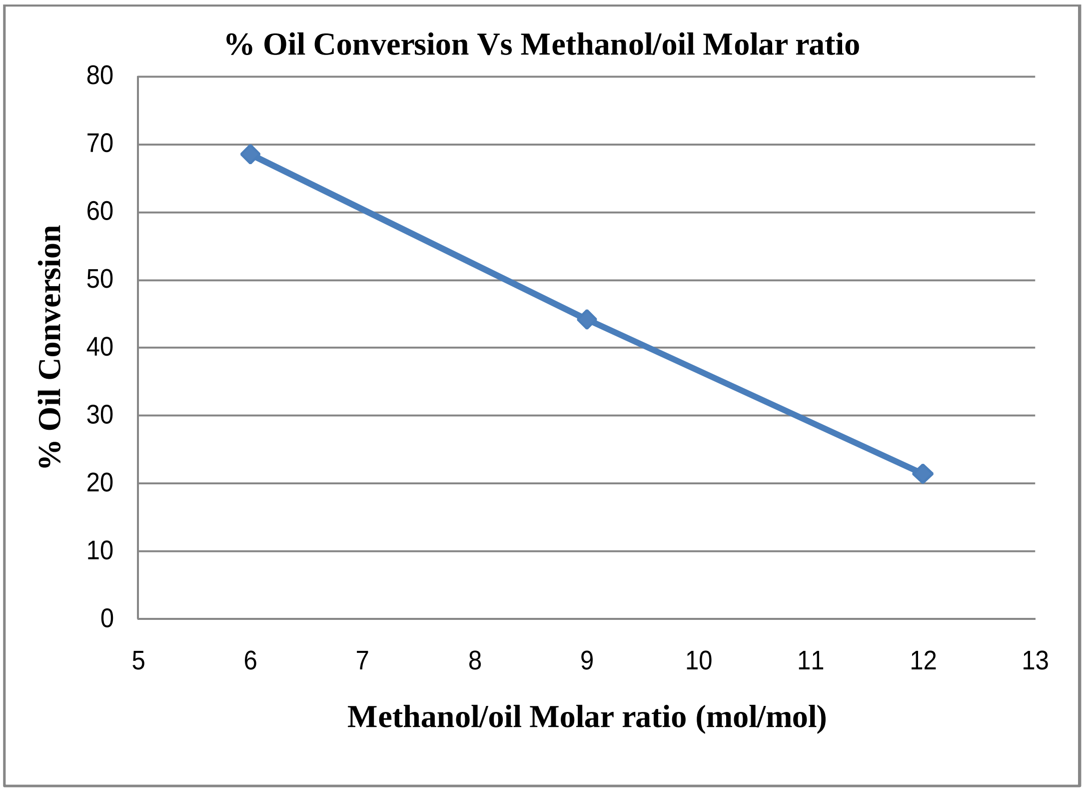


Figure 4.14: Influence of methanol/oil molar ratio on the conversion. Reaction conditions: Sunflower oil 50g, reaction time 5.33 hr, catalyst amount 10%, and reaction temperature 70°C.

4.4 Kinetics of transesterification

Although the importance of biodiesel as an alternative fuel has grown during the last twenty years, the chemical kinetics of transesterification, very important for process design, remain controversial. Kinetics describes the rate of chemical reactions. Rate equations are typically written in terms of the concentration of the reactants. The transesterification reaction is a reversible reaction, and proceeds in three consecutive steps. The overall reaction, assumed to be single step (ignoring/ neglecting intermediate steps), was considered to develop a kinetic rate equation.

The reaction kinetics was developed based on the experimental data obtained at three different temperatures which are 60ºC, 70ºC and 100ºC. Figure 4.15 shows that as the reaction temperature increases, the conversion also increases.

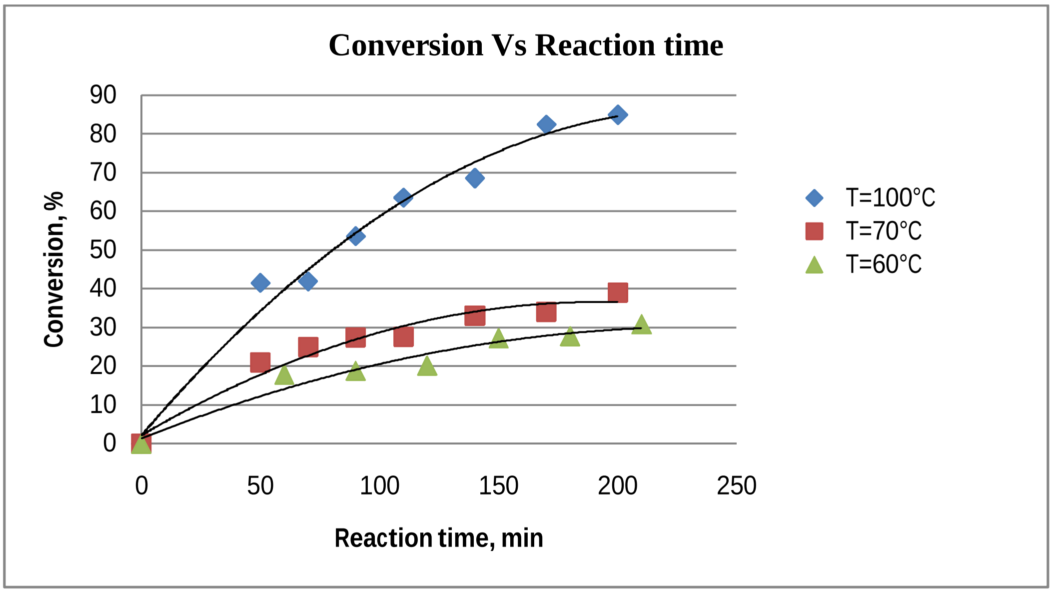


Figure 4.15: Effect of temperature. Reaction conditions: Sunflower oil 50g, molar ratio of methanol to oil=6:1, catalyst amount=10% (wt/wt), and reaction time=3.33hr.

The kinetic model used is Pseudo-homogeneous model. Equation 4.1 shows the generalized transesterification reaction, where A is triglycerides, B is methanol, C is

FAME and D is glycerol. The equation also shows the stoichiometric relationship between the reactants and the products.

$$A+3B \rightarrow 3C+D \tag{4.1}$$

For batch reactor, the general rate equation for the chemical equation 4.1 is,

$$-r_A=-\frac{dC_A}{dt}=kC_A^{\alpha}C_B^{\beta} \tag{4.2}$$

Because the concentration of methanol is 6 times the initial concentration of oil, its concentration is essentially constant

$$C_B=C_{BO} \tag{4.3}$$

Substituting for $C_B$in Equation 4.4.3

$$-r_A=-\frac{dC_A}{dt}=kC_A^{\alpha}C_{Bo}^{\beta}$$

$$-r_A=-\frac{dC_A}{dt}=k'C_A^{\alpha} \tag{4.4}$$

Where,

$-r_A=-\frac{dC_A}{dt}$ = the consumption of reactant A per unit time

k’ = rate constant

C_A = concentration of A after time t

C_B = concentration of B after time t

= reaction order of reactant A

= reaction order of reactant B

Also,

$$C_A=C_{AO}(1-X) \tag{4.5}$$

$$C_B=C_{BO}(\theta_B-3X) \tag{4.6}$$

$$\theta_B = \frac{C_{BO}}{C_{AO}} \tag{4.7}$$

Where,

C_{AO}= initial concentration of A

C_{BO}= initial concentration of B

X= conversion

θ_B= ratio of C_{BO} to C_{AO}

The rate law parameters from concentration-time data obtained in batch experiments were determined using nonlinear regression. The Polymath regression program was used to find the values of   and k' that minimizing s². Recalling Equation 4.4

$$-\frac{dC_A}{dt} = k'C_A^{\alpha}$$

Where,

$$k = \frac{k'}{C_{BO}}$$

and integrating with the initial condition when t=0 and C_A=C_{AO} for α≠1

$$t = \frac{1}{k'}\frac{C_{AO}^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \tag{4.8}$$

Substituting for the initial concentration $C_{AO}\ =\ 8.16\ \times\ 10$ mol/mL

$$t = \frac{1}{k'}\frac{(8.16\times10^{-4})^{(1-\alpha)} - C_A^{(1-\alpha)}}{(1-\alpha)} \tag{4.9}$$

The Polymath results are shown in Appendix C. Table 4.5 shows the results obtained from the nonlinear regression based on four guesses.

Table 4.5: Regression Data

Guess 1				
Temperature °C	**α**	**k'**	**R^2**	**k(ml$^{0.785}$mol$^{-0.785}$min^{-1})**
100	0.785	1.73E-03	0.983	3.45E-01
70	0.785	6.82E-04	0.939	1.36E-01
60	0.785	4.27E-04	0.926	8.51E-02
Guess 2				
Temperature °C	**α**	**k'**	**R^2**	**k(ml$^{0.38}$mol$^{-0.38}$min^{-1})**
100	0.38	7.53E-05	0.959	1.50E-02
70	0.38	3.11E-05	0.958	6.20E-03
60	0.38	2.17E-05	0.936	4.33E-03
Guess 3				
Temperature °C	**α**	**k'**	**R^2**	**k(ml$^{0.17}$mol$^{-0.17}$min^{-1})**
100	0.17	1.51E-05	0.933	3.00E-03
70	0.17	6.36E-06	0.954	1.27E-03
60	0.17	4.65E-06	0.937	9.26E-04
Guess 4				
Temperature °C	**α**	**k'**	**R^2**	**K(ml$^{0.6}$mol$^{-0.6}$min^{-1})**
100	0.6	4.11E-04	0.977	8.20E-02
70	0.6	1.66E-04	0.952	3.30E-02
60	0.6	1.09E-04	0.932	2.18E-02

The results with the highest R² were chosen as the correct answer. Therefore, results obtained from guess four are chosen, the order of reaction, α=0.6 and the rate constants, k are 8.20, 3.30, and 2.18 for the temperature of 100, 70, and 60ºC respectively.

The activation energy, E, is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of the Arrhenius Equation, Equation 4.10 is obtained.

$$\ln k_A = \ln A - \frac{E}{R}\,\frac{1}{T} \qquad (4.10)$$

Where

A= pre-exponential factor or frequency factor

E= activation energy, J/mol or cal/mol

R= gas constant=8.314 J/mol.K=1.987 cal/mol. K

T= absolute temperature, K

Based on the data given in Table 4.6. The activation energy can be found from a plot of as a function of (1/T). Figure 4.16 shows the plot of ln k Vs 1/T.

Table 4.6: Data for plotting ln k Vs 1/T.

Temperature, K	**k**	**ln k**	**(1/T) K^{-1}**
373.15	8.20E-02	-2.502	0.0027
343.15	3.30E-02	-3.411	0.0029
333.15	2.18E-02	-3.825	0.0030

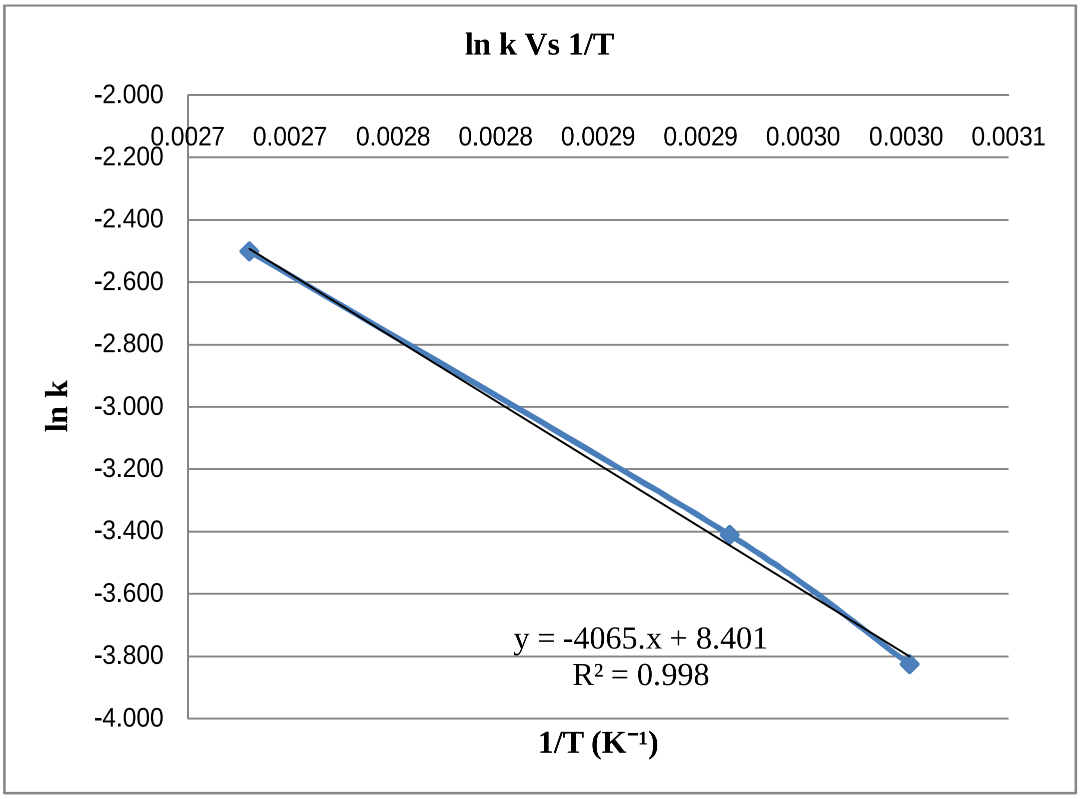


Figure 4.16: Plot of ln k Vs 1/T.

The high R^2-value (0.998) is indicative of a good fit between the data points calculated from the experimental data and the trend line fitted to the data.

The equation for the best fit of the data is

$$\ln k_A = \frac{4065}{T} + 8.401 \qquad (4.11)$$

From the slope of the line given in Figure 4.16

$$-\frac{E}{R} = -4065\ K$$

$$E = (4065\ K)R = (4065\ K)(8.314\ \frac{J}{mol.K})$$

$$E = 33.796\ \frac{KJ}{mol}$$

From the Equation 4.11,

$\ln A=8.401$

Taking the antilog

$A=4.451\times10^{3}\text{min}^{-1}$

The Arrhenius Equation is:

$$k=4.451\times10^{3}\exp\ -\frac{4065\ \text{K}}{T} \qquad (4.12)$$

The activation energy determined is small. Reactions with high activation energies are very temperature-sensitive and reactions with low activation energies are relatively temperature-insensitive. In the case of the transesterification of Castor oil by methanol with KOH/Al2O3 as catalyst, the activation energy is 43.03 KJ/mol (Perin, 2008) which is more than the activation energy obtained from this study.

A good correlation between the experimental data and the modeled data was obtained and it is shown in Figures 4.17-4.19.

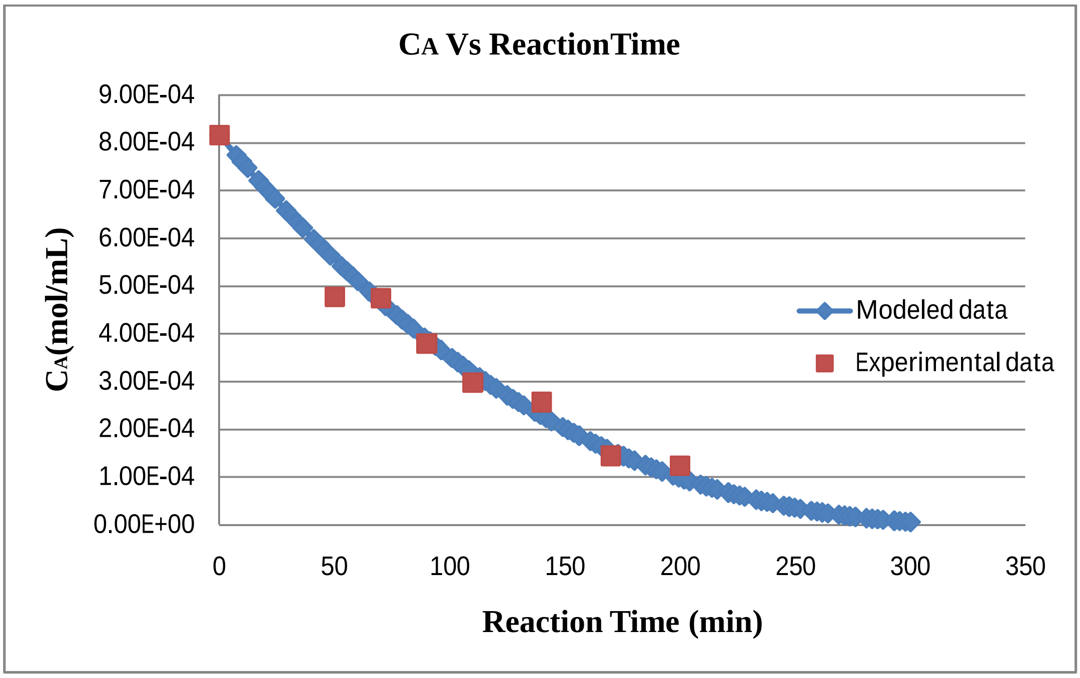


Figure 4.17: Concentration of oil (C_A) Vs Reaction time at T=373.15 K. Reaction conditions: Sunflower oil 50g, molar ratio of methanol to oil=6:1, catalyst amount=10% (wt/wt), and reaction time= 3.33hr.

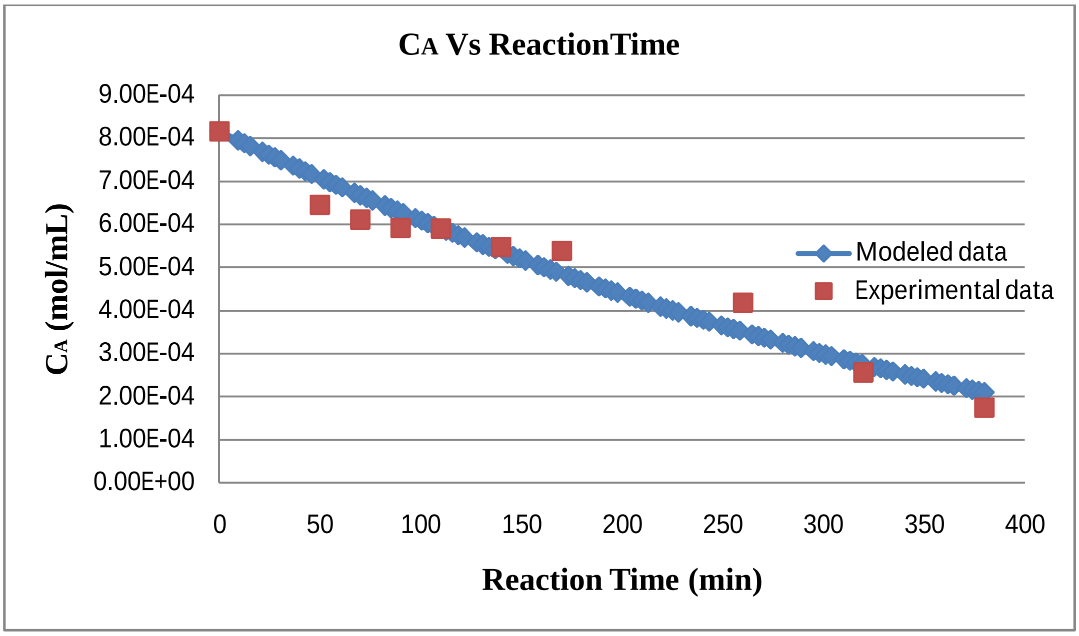


Figure 4.18: Concentration of oil (C_A) Vs Reaction time at T=343.15 K. Reaction conditions: Sunflower oil 50g, molar ratio of methanol to oil=6:1, catalyst amount=10% (wt/wt), and reaction time= 3.33hr.

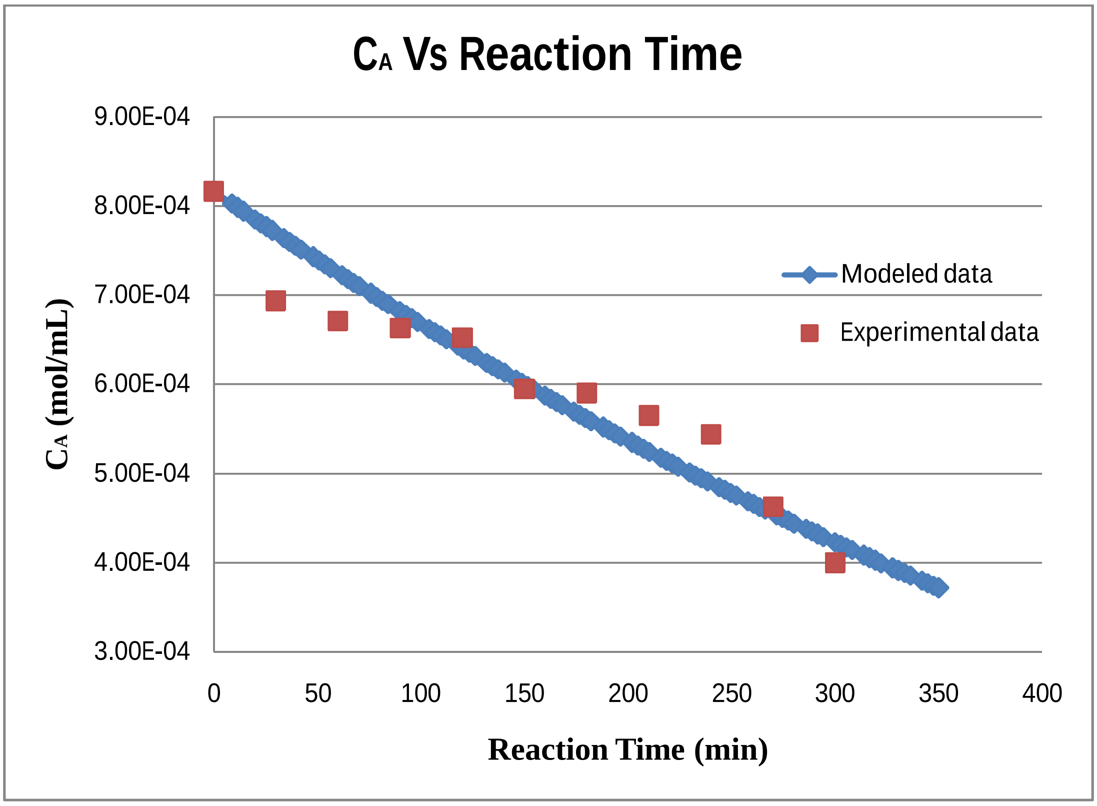


Figure 4.19: Concentration of oil (C_A) Vs Reaction time at T=333.15 K. Reaction conditions: Sunflower oil 50g, molar ratio of methanol to oil=6:1, catalyst amount=10% (wt/wt), and reaction time= 3.33hr.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

Silica gel loaded with sulfuric acid was found to be strong solid acid catalyst for the transesterification of Sunflower oil with methanol. The most important variables that influence transesterification reaction time and conversion:

- Reaction temperature
- Ratio of alcohol to oil
- Amount of catalyst needed.

It was observed that increase in oil temperature marginally increases the percentage oil to biodiesel conversion as well as the biodiesel recovery. However, the tests were conducted up to 100°C only, as higher temperatures may result in methanol loss in the batch process. The rate of reaction is strongly influenced by the reaction temperature. Further increase in temperature is reported to have a negative effect on the conversion. When the reaction was carried out at 100°C, with a molar ratio of methanol to oil of 6:1, a reaction time of 3.33hr and catalyst amount 10%, the highest conversion reached 84%. It was observed from the kinetic study of transesterification process for all the temperature, order of the reaction is 0.600 and reaction rate constant is 8.20E-02 $\text{ml}^{0.6}\text{mol}^{-0.6}$. Activation energy is 33.796 $\frac{\text{KJ}}{\text{mol}}$ and frequency factor is $4.451 \times 10^{3}\text{min}^{-1}$. The experimental data is well fitted to the Pseudo-homogeneous kinetic model.

5.2 Recommendation

Based on the present study, we make the following recommendations:

- In the catalyst study, sulfuric acid impregnated along with silica gel proved to be an effective transesterification catalyst. However, we still observed some lacking of the catalyst. This opens up new doors to improve the catalyst stability for example by adding some thermal stability agent to the catalyst.
- In the activity studies, we may perform the reaction at the continuous flow reactors.
- In the kinetic model studies, in many industrial reactions, the overall rate of reaction is limited by the rate of mass transfer of reactions between the bulk fluid and the catalytic surface. By mass transfer, we mean any process in which diffusion play in role. We should model the effect of the absorption of the reactant.

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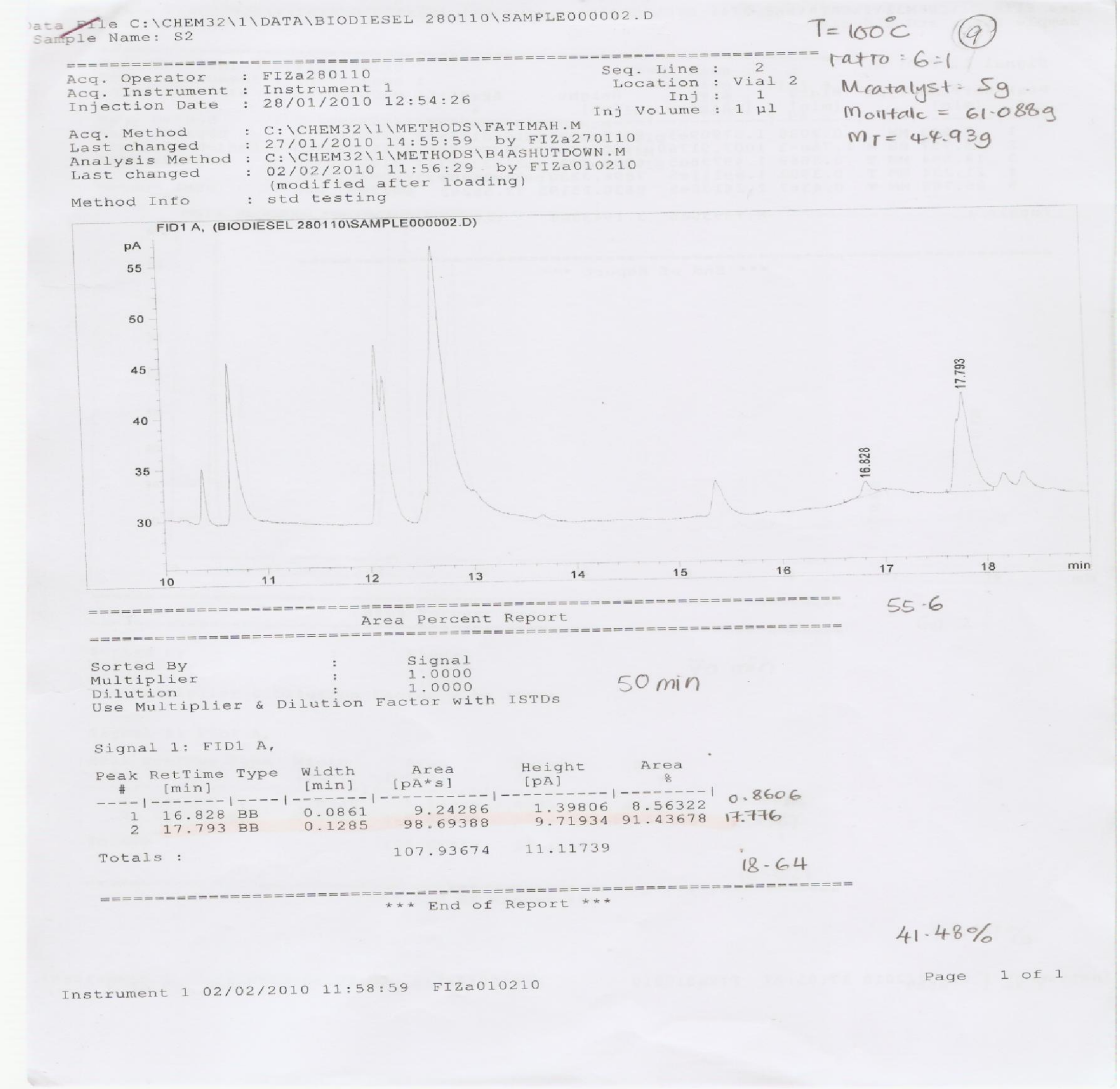
APPENDIX A

GC CHROMATROGRAM

APPENDIX A

Chromatogram for sample at optimum condition



```
ata File C:\CHEM32\1\DATA\BIODIESEL 280110\SAMPLE000002.D
Sample Name: S2

=====================================================================
Acq. Operator     : FIZa280110                    Seq. Line :    2
Acq. Instrument   : Instrument 1                   Location : Vial 2
Injection Date    : 28/01/2010 12:54:26                 Inj :    1
                                                 Inj Volume : 1 µl
Acq. Method       : C:\CHEM32\1\METHODS\FATIMAH.M
Last changed      : 27/01/2010 14:55:59  by FIZa270110
Analysis Method   : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
Last changed      : 02/02/2010 11:56:29  by FIZa010210
                    (modified after loading)
Method Info       : std testing
```

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [pA*s]        [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  16.828 BB    0.0861    9.24286    1.39806  8.56322
   2  17.793 BB    0.1285   98.69388    9.71934 91.43678

Totals :                   107.93674   11.11739

=====================================================================
                        *** End of Report ***

                                                          Page   1 of 1
Instrument 1 02/02/2010 11:58:59  FIZa010210
```

T= 100°C ⑨

ratio : 6:1

Mcatalyst = 5g

Moil+alc = 61.088g

MT = 44.93g

55.6

50 min

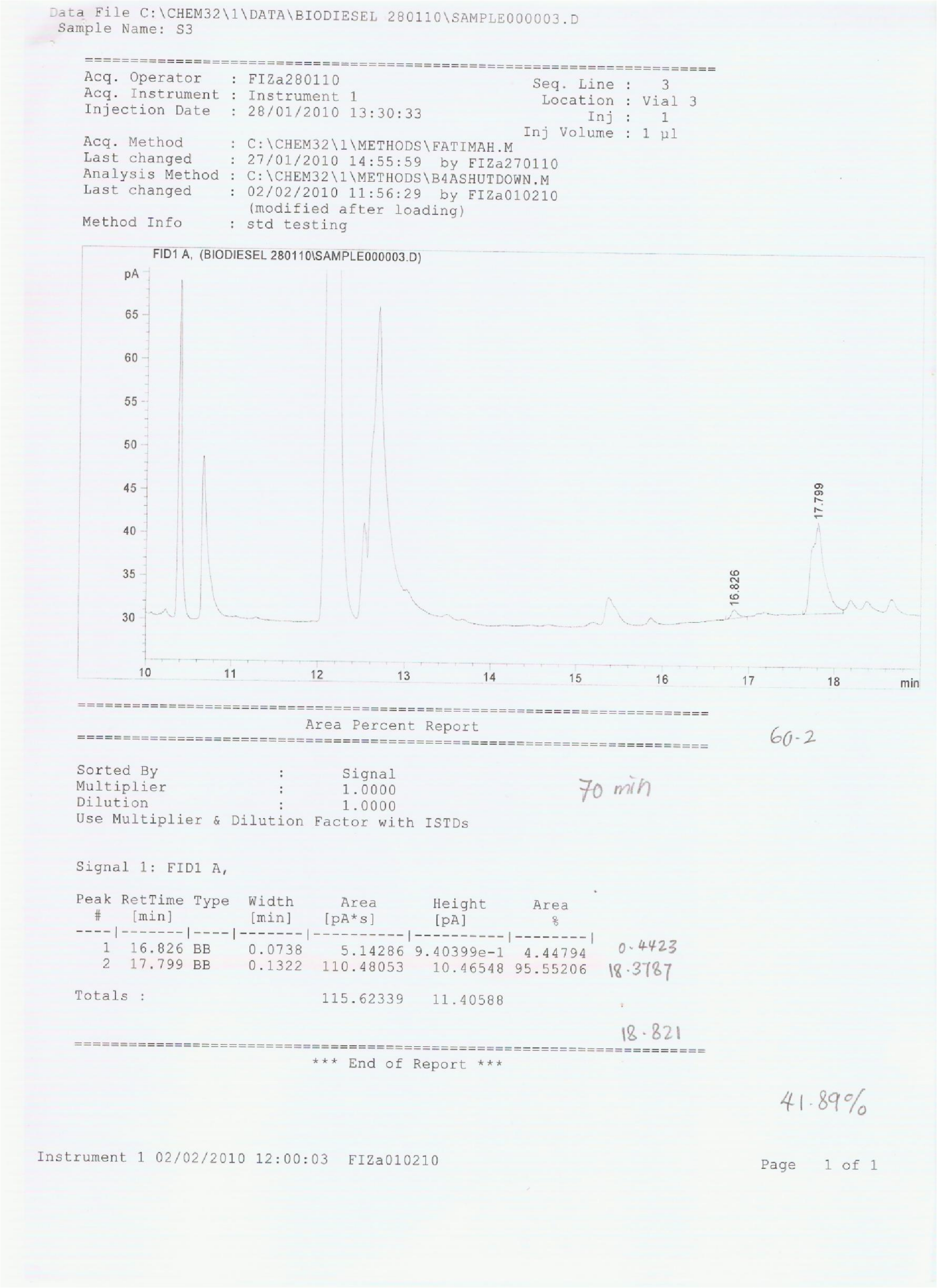
0.8606

17.776

18.64

41.48%

Appendix A1: GC chromatogram sample 1



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Sample Name: S3

=====================================================================
Acq. Operator   : FIZa280110                      Seq. Line :   3
Acq. Instrument : Instrument 1                     Location : Vial 3
Injection Date  : 28/01/2010 13:30:33                   Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
Last changed    : 27/01/2010 14:55:59  by FIZa270110
Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
Last changed    : 02/02/2010 11:56:29  by FIZa010210
                  (modified after loading)
Method Info     : std testing
```

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  16.826 BB    0.0738    5.14286 9.40399e-1  4.44794
   2  17.799 BB    0.1322  110.48053   10.46548 95.55206

Totals :                   115.62339   11.40588

=====================================================================
                         *** End of Report ***

Instrument 1 02/02/2010 12:00:03  FIZa010210                  Page    1 of 1
```

60-2

70 min

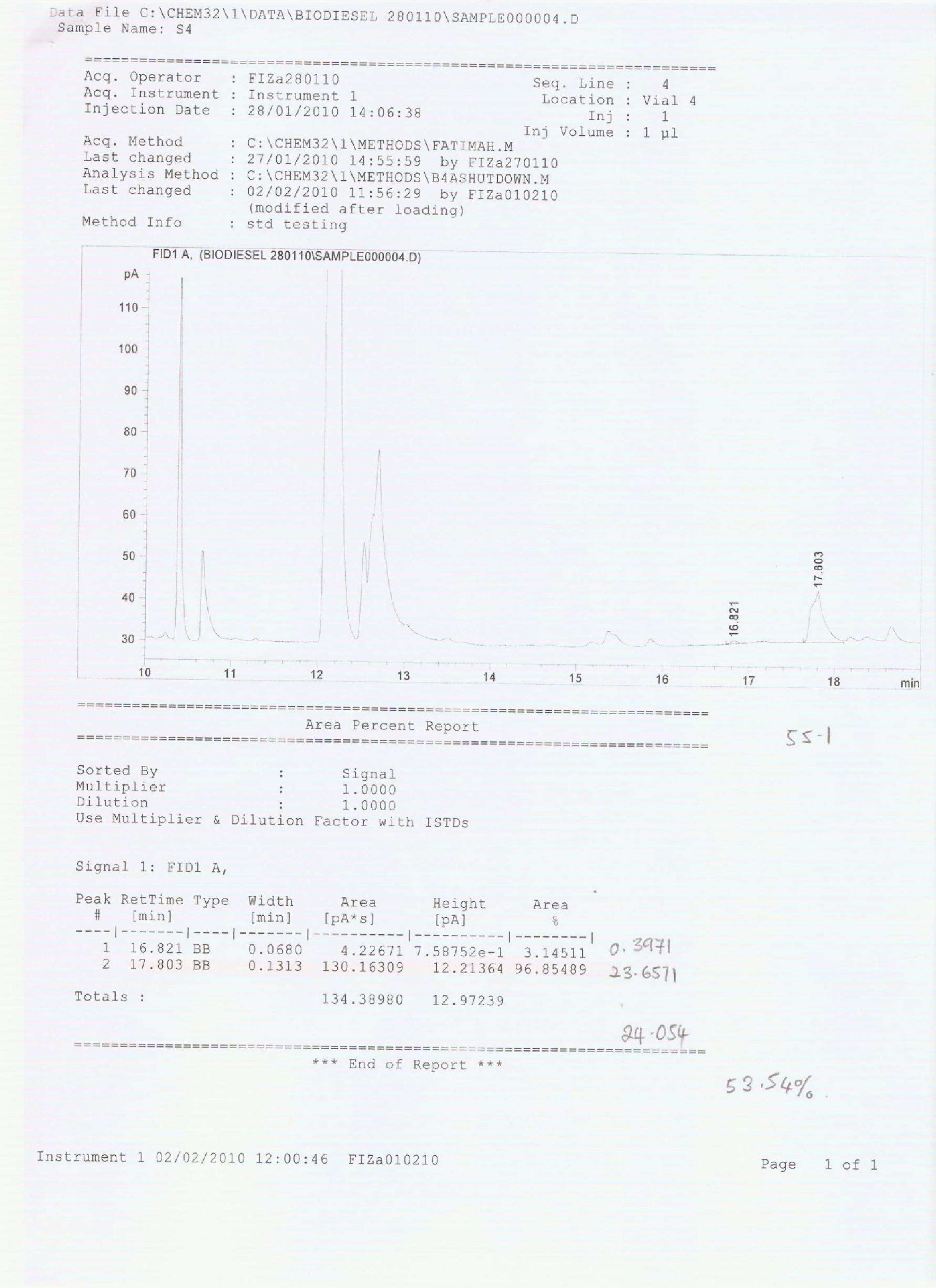
0.4423

18.3787

18.821

41.89%

Appendix A2: GC chromatogram sample 2



```
Data File C:\CHEM32\1\DATA\BIODIESEL 280110\SAMPLE000004.D
Sample Name: S4

    =====================================================================
    Acq. Operator   : FIZa280110                         Seq. Line :    4
    Acq. Instrument : Instrument 1                        Location : Vial 4
    Injection Date  : 28/01/2010 14:06:38                      Inj :    1
                                                        Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 27/01/2010 14:55:59  by FIZa270110
    Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed    : 02/02/2010 11:56:29  by FIZa010210
                      (modified after loading)
    Method Info     : std testing
```

```
    =====================================================================
                          Area Percent Report
    =====================================================================          55·1

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

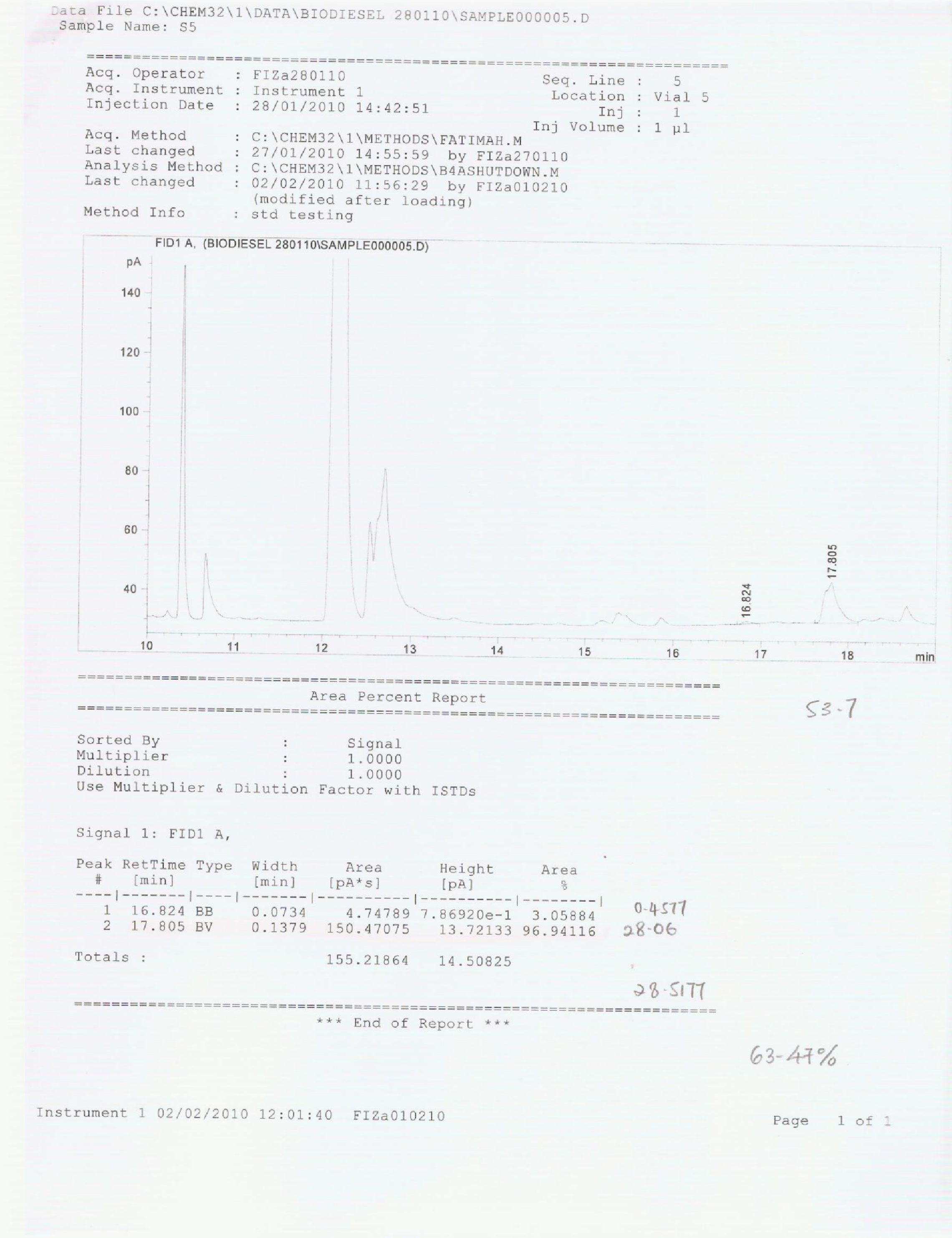
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1  16.821 BB    0.0680    4.22671 7.58752e-1  3.14511  0.3971
       2  17.803 BB    0.1313  130.16309   12.21364 96.85489  23.6571

    Totals :                   134.38980   12.97239

                                                                24·054
    =====================================================================
                          *** End of Report ***
                                                                          53.54%

Instrument 1 02/02/2010 12:00:46   FIZa010210                       Page    1 of 1
```

Appendix A3: GC chromatogram sample 3



```
Data File C:\CHEM32\1\DATA\BIODIESEL 280110\SAMPLE000005.D
Sample Name: S5

   =====================================================================
   Acq. Operator   : FIZa280110                          Seq. Line :    5
   Acq. Instrument : Instrument 1                         Location : Vial 5
   Injection Date  : 28/01/2010 14:42:51                       Inj :    1
                                                        Inj Volume : 1 µl
   Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
   Last changed    : 27/01/2010 14:55:59  by FIZa270110
   Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
   Last changed    : 02/02/2010 11:56:29  by FIZa010210
                     (modified after loading)
   Method Info     : std testing
```

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

   Sorted By             :      Signal
   Multiplier            :      1.0000
   Dilution              :      1.0000
   Use Multiplier & Dilution Factor with ISTDs


   Signal 1: FID1 A,

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]        [min]   [pA*s]      [pA]        %
   ----|-------|----|-------|----------|----------|--------|
      1  16.824 BB    0.0734    4.74789 7.86920e-1  3.05884
      2  17.805 BV    0.1379  150.47075   13.72133 96.94116

   Totals :                   155.21864   14.50825

   =====================================================================
                         *** End of Report ***


Instrument 1 02/02/2010 12:01:40  FIZa010210                    Page    1 of 1
```

53.7

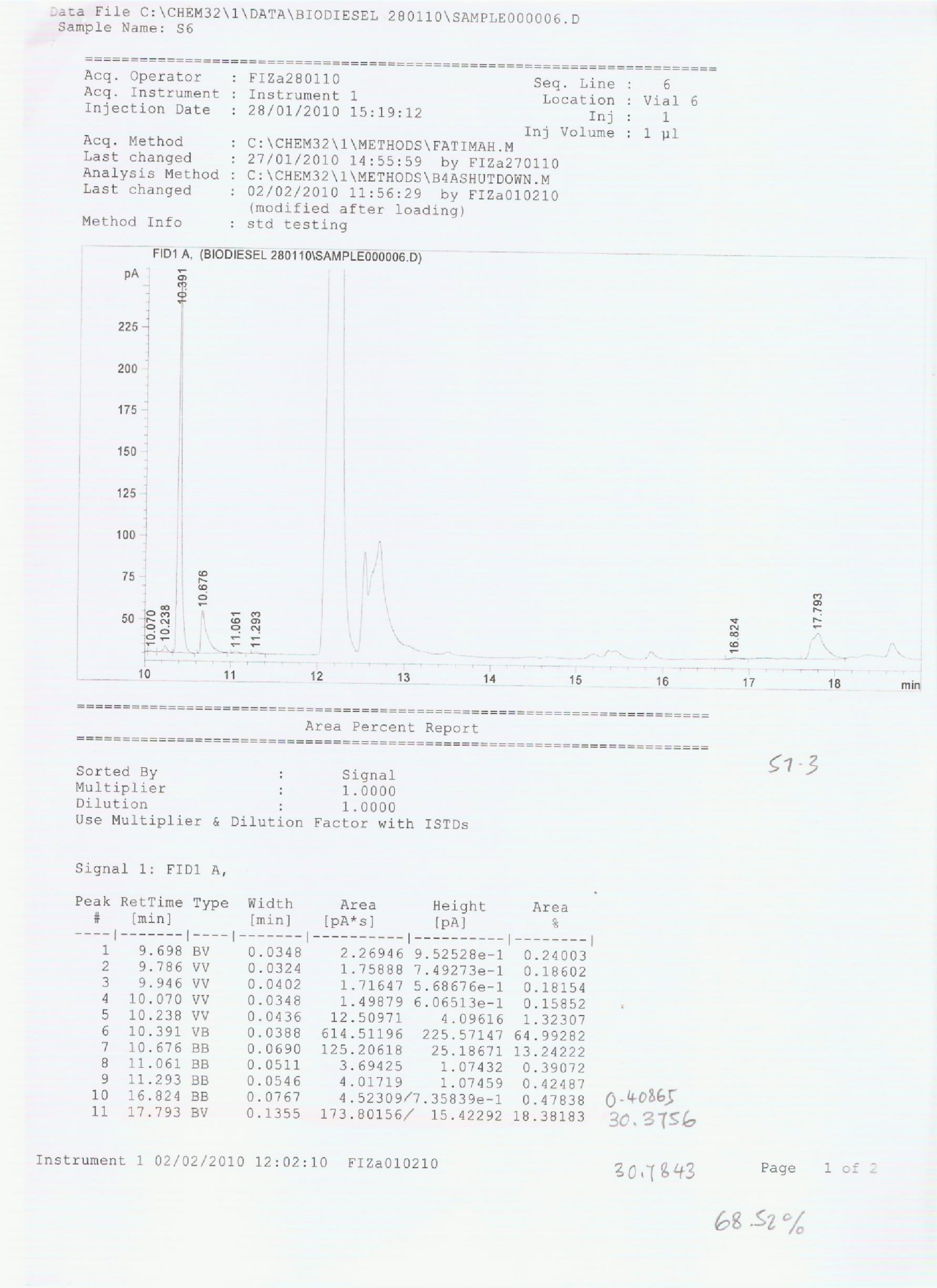
0.4577

28.06

28.5177

63.47%

Appendix A4: GC chromatogram sample 4



```
Data File C:\CHEM32\1\DATA\BIODIESEL 280110\SAMPLE000006.D
 Sample Name: S6

     =================================================================
     Acq. Operator   : FIZa280110
     Acq. Instrument : Instrument 1                   Seq. Line :   6
     Injection Date  : 28/01/2010 15:19:12             Location : Vial 6
                                                           Inj :   1
                                                    Inj Volume : 1 µl
     Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
     Last changed    : 27/01/2010 14:55:59  by FIZa270110
     Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
     Last changed    : 02/02/2010 11:56:29  by FIZa010210
                       (modified after loading)
     Method Info     : std testing

     =================================================================
                           Area Percent Report
     =================================================================
                                                                  51.3
     Sorted By             :      Signal
     Multiplier            :      1.0000
     Dilution              :      1.0000
     Use Multiplier & Dilution Factor with ISTDs

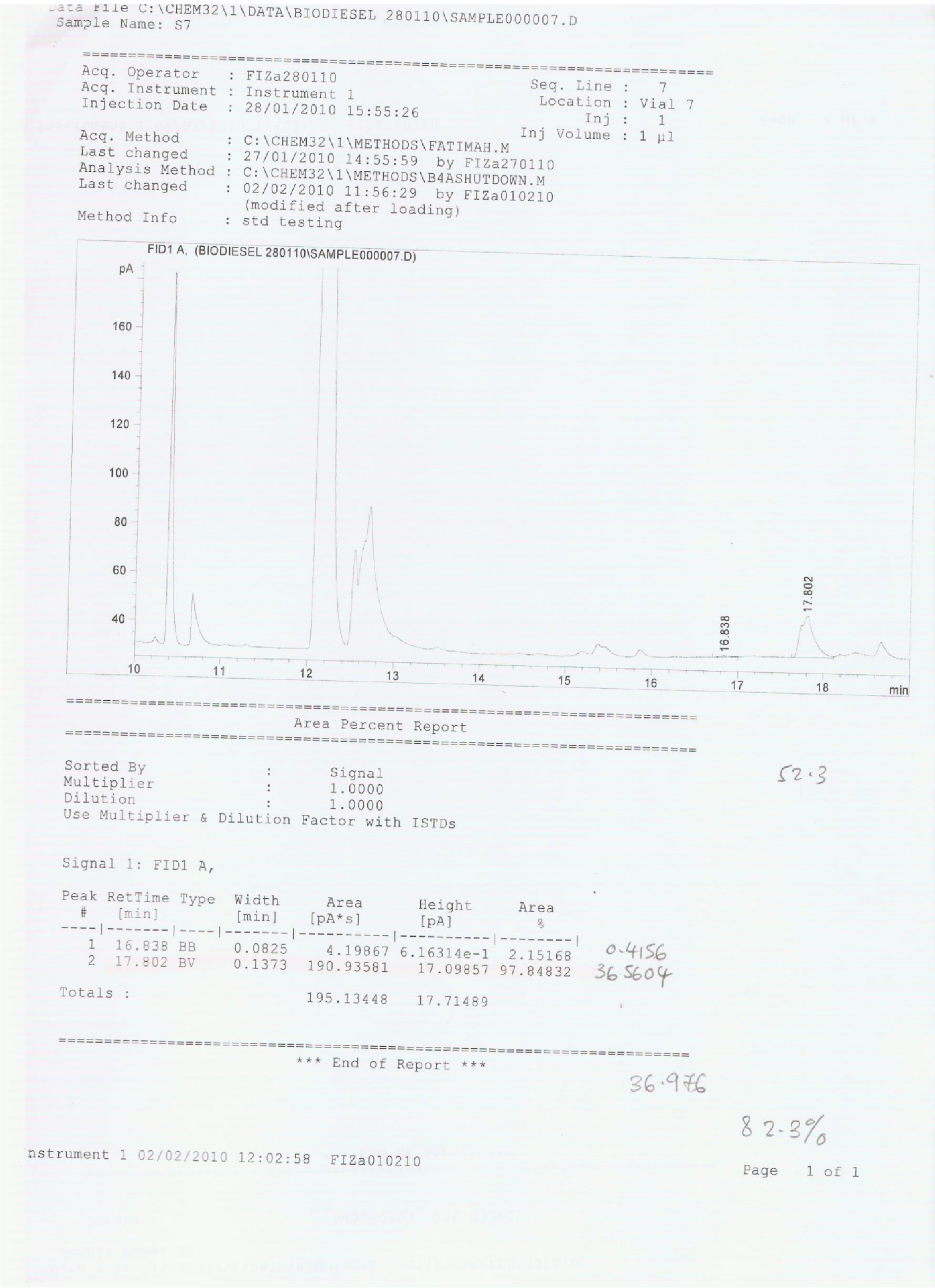

     Signal 1: FID1 A,

     Peak RetTime Type  Width     Area      Height     Area
       #   [min]        [min]   [pA*s]       [pA]        %
     ----|-------|----|-------|----------|----------|--------|
        1   9.698 BV    0.0348    2.26946 9.52528e-1  0.24003
        2   9.786 VV    0.0324    1.75888 7.49273e-1  0.18602
        3   9.946 VV    0.0402    1.71647 5.68676e-1  0.18154
        4  10.070 VV    0.0348    1.49879 6.06513e-1  0.15852
        5  10.238 VV    0.0436   12.50971    4.09616  1.32307
        6  10.391 VB    0.0388  614.51196  225.57147 64.99282
        7  10.676 BB    0.0690  125.20618   25.18671 13.24222
        8  11.061 BB    0.0511    3.69425    1.07432  0.39072
        9  11.293 BB    0.0546    4.01719    1.07459  0.42487
       10  16.824 BB    0.0767    4.52309/7.35839e-1  0.47838  0-40865
       11  17.793 BV    0.1355  173.80156/  15.42292 18.38183  30.3756

Instrument 1 02/02/2010 12:02:10  FIZa010210                 30.7843      Page   1 of 2

                                                                    68.52%
```

Appendix A5: GC chromatogram sample 5



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ata File C:\CHEM32\1\DATA\BIODIESEL 280110\SAMPLE000007.D
Sample Name: S7

    =====================================================================
    Acq. Operator   : FIZa280110
    Acq. Instrument : Instrument 1                  Seq. Line :   7
    Injection Date  : 28/01/2010 15:55:26            Location : Vial 7
                                                          Inj :   1
                                                   Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 27/01/2010 14:55:59  by FIZa270110
    Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed    : 02/02/2010 11:56:29  by FIZa010210
                      (modified after loading)
    Method Info     : std testing
```

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  16.838 BB    0.0825    4.19867 6.16314e-1  2.15168
   2  17.802 BV    0.1373  190.93581   17.09857 97.84832

Totals :                   195.13448   17.71489

=====================================================================
                         *** End of Report ***

nstrument 1 02/02/2010 12:02:58  FIZa010210                          Page    1 of 1
```

52.3

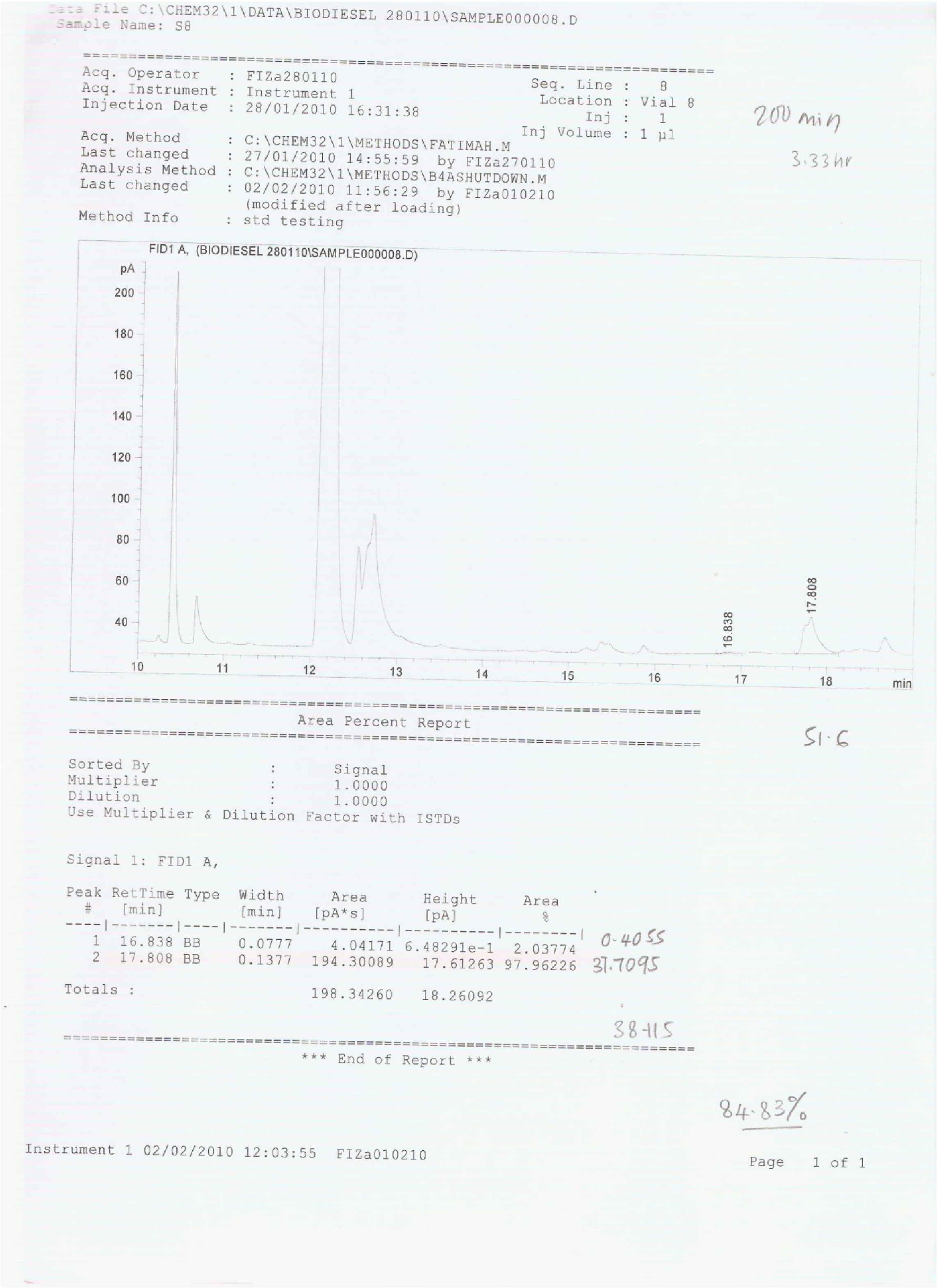
0.4156

36.5604

36.976

82.3%

Appendix A6: GC chromatogram sample 6



```
Data File C:\CHEM32\1\DATA\BIODIESEL 280110\SAMPLE000008.D
Sample Name: S8

    =====================================================================
    Acq. Operator    : FIZa280110
    Acq. Instrument  : Instrument 1                     Seq. Line :   8
    Injection Date   : 28/01/2010 16:31:38               Location : Vial 8
                                                              Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method      : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed     : 27/01/2010 14:55:59  by FIZa270110
    Analysis Method  : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed     : 02/02/2010 11:56:29  by FIZa010210
                       (modified after loading)
    Method Info      : std testing
```

200 min

3.33hr

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

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1  16.838 BB    0.0777    4.04171 6.48291e-1  2.03774
       2  17.808 BB    0.1377  194.30089   17.61263 97.96226

    Totals :                   198.34260   18.26092

    =====================================================================
                            *** End of Report ***


Instrument 1 02/02/2010 12:03:55  FIZa010210                      Page   1 of 1
```

51·6

0·4055

37.7095

38·115

84·83%

Appendix A7: GC chromatogram sample 7

APPENDIX B

TYPICAL ANALYSIS CALCULATION

APPENDIX B

Typical Analysis Calculation

A calibration curve would be in area under each peak vs. concentration for each ester group, as can be seen in figure 4.2.1. From the calibration curve with an original know mass of sample we can calculate the quantity of that compound and its relative proportions in the sample. As is as follow; Lets say for example sake the area under the curve obtained from the GC, of the methyl palmitate, sums to 39.773 counts and the original mass of sample was 67.7 mg.

$y=mx+C$
(4.13)

$39.773=0.187x$

$x=212.69\ \mu g/mL$

We know we had 10 mL to start with so the mass of methyl palmitate is

$x=2126.90\ \mu g$

With an initial mass of sample we can calculate the percentage of methyl palmitate in the sample. Percentage of methyl palmitate in the sample

$$=\frac{2126.90\mu g}{67700\mu g}\times 100=3.14\%$$

The total weight of methyl esters obtained was calculated using following formula:

Total weight of methyl esters obtained= $\sum_i m\times$(mass of oil + mass of alcohol)
(4.14)

Where:

i= methyl palmitate, methyl oleate and methyl linoleate

The conversion of oil in each experiment was calculated from the content in methyl esters of biodiesel as analysed by GC. Thus, based on the weight of each methyl easters obtained, the % oil conversion has been calculated using following formula:

$$\text{\% oil conversion}=\frac{\text{Total weight of methly esters obtained}}{\text{Theoretical weight of methyl esters calculated}}\text{x100} \qquad (4.15)$$

Where:

The theoretical weight of methyl esters was calculated using following formula:

$$\text{Theoretical weight of methyl esters}_{i}=\frac{\text{Weight of oilx3}}{\text{MW of oil}}\text{x p x MW of methyl esters}_{i} \qquad (4.16)$$

MW= Molecular weight

P = Percentage of Fatty acid methyl ester(FAME) in the Biodiesel

(The factor 3 appears in the formula since each triglyceride molecule yields three alkyl ester molecules.)

APPENDIX C

POLYMATH RESULTS

APPENDIX C

POLYMATH RESULTS

Guess 1

T= 100°C

POLYMATH Results
POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.785)-CA^(1-0.785))/(k*(1-0.785))

Variable	Ini guess	Value	95% confidence
k	2.0E-04	0.0017318	1.041E-04

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9825514
R^2adj = 0.9825514
Rmsd = 2.8593081
Variance = 74.748735

General
Sample size = 8
Model vars = 1
Indep vars = 1
Iterations = 8

T= 70°C

```
POLYMATH Results
POLYMATH Report  03-20-2010

Nonlinear regression (L-M)

 Model: t =  (8.16e-4^(1-0.785 )-CA^(1-0.785 ))/(k*(1-0.785 ))

 Variable     Ini guess    Value     95% confidence
 k            4.0E-04      6.82E-04  7.653E-05

 Nonlinear regression settings
 Max # iterations = 64

 Precision
 R^2       =  0.9385253
 R^2adj    =  0.9385253
 Rmsd      =  9.200248
 Variance  =  940.49515

 General
 Sample size   = 10
 # Model vars  = 1
 # Indep vars  = 1
 # Iterations  = 5
```

T= 60°C

POLYMATH Results

POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.785)-CA^(1-0.785))/(k*(1-0.785))

Variable	Ini guess	Value	95% confidence
k	4.0E-04	4.269E-04	4.342E-05

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9257274
R^2adj = 0.9257274
Rmsd = 7.8590761
Variance = 686.27863

General
Sample size = 10
Model vars = 1
Indep vars = 1
Iterations = 4

Guess 2

T=100°C

POLYMATH Results
POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.38)-CA^(1-0.38))/(k*(1-0.38))

Variable	Ini guess	Value	95% confidence
k	5.0E-05	7.528E-05	6.973E-06

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9588692
R^2adj = 0.9588692
Rmsd = 4.389993
Variance = 176.2015

General
Sample size = 8
Model vars = 1
Indep vars = 1
Iterations = 5

T= 70°C

```
POLYMATH Results
POLYMATH Report  03-20-2010

Nonlinear regression (L-M)

 Model: t =  (8.16e-4^(1-0.38 )-CA^(1-0.38 ))/(k*(1-0.38 ))

 Variable     Ini guess     Value     95% confidence
 k            3.0E-05     3.109E-05    2.877E-06

 Nonlinear regression settings
 Max # iterations = 64

 Precision
 R^2        =  0.9579053
 R^2adj     =  0.9579053
 Rmsd       =  7.6131628
 Variance  =  644.00276

 General
 Sample size   = 10
 # Model vars  = 1
 # Indep vars  = 1
 # Iterations  = 3
```

T= 60ºC

POLYMATH Results
POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.38)-CA^(1-0.38))/(k*(1-0.38))

Variable	Ini guess	Value	95% confidence
k	1.0E-05	2.171E-05	2.053E-06

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9356038
R^2adj = 0.9356038
Rmsd = 7.3179174
Variance = 595.02128

General
Sample size = 10
Model vars = 1
Indep vars = 1
Iterations = 6

Guess 3

T= 100ºC

POLYMATH Results

POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.17)-CA^(1-0.17))/(k*(1-0.17))

Variable	Ini guess	Value	95% confidence
k	1.0E-05	1.507E-05	1.794E-06

Nonlinear regression settings

Max # iterations = 64

Precision

R^2 = 0.93252

R^2adj = 0.93252

Rmsd = 5.6229941

Variance = 289.07943

General

Sample size = 8

Model vars = 1

Indep vars = 1

Iterations = 5

T= 70°C

```
POLYMATH Results
POLYMATH Report  03-20-2010

Nonlinear regression (L-M)

 Model: t =  (8.16e-4^(1-0.17)-CA^(1-0.17))/(k*(1-0.17))

 Variable     Ini guess    Value     95% confidence
 k            3.0E-06     6.362E-06   6.192E-07

 Nonlinear regression settings
 Max # iterations = 64

 Precision
 R^2       =  0.9535165
 R^2adj    =  0.9535165
 Rmsd      =  8.0001925
 Variance  =  711.14534

 General
 Sample size   = 10
 # Model vars  = 1
 # Indep vars  = 1
 # Iterations  = 6
```

T= 60ºC

POLYMATH Results
POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.17)-CA^(1-0.17))/(k*(1-0.17))

Variable	Ini guess	Value	95% confidence
k	5.0E-06	4.645E-06	4.355E-07

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9367323
R^2adj = 0.9367323
Rmsd = 7.2535091
Variance = 584.59326

General
Sample size = 10
Model vars = 1
Indep vars = 1
Iterations = 4

Guess 4

T=100°C

```
POLYMATH Results
POLYMATH Report  03-20-2010

Nonlinear regression (L-M)

 Model: t =  (8.16e-4^(1-0.60)-CA^(1-0.60))/(k*(1-0.60))

 Variable     Ini guess    Value     95% confidence
 k            4.0E-04     4.11E-04   2.829E-05

 Nonlinear regression settings
 Max # iterations = 64

 Precision
 R^2        =  0.9771689
 R^2adj     =  0.9771689
 Rmsd       =  3.2707208
 Variance   =  97.806761

 General
 Sample size   = 8
 # Model vars  = 1
 # Indep vars  = 1
 # Iterations  = 3
```

T= 70°C

```
POLYMATH Results
POLYMATH Report  03-20-2010

Nonlinear regression (L-M)

 Model: t =  (8.16e-4^(1-0.60)-CA^(1-0.60))/(k*(1-0.60))

 Variable     Ini guess     Value     95% confidence
 k            4.0E-04     1.656E-04    1.632E-05

 Nonlinear regression settings
 Max # iterations = 64

 Precision
 R^2        =  0.9523606
 R^2adj     =  0.9523606
 Rmsd       =  8.0990531
 Variance   =  728.82956

 General
 Sample size    = 10
 # Model vars   = 1
 # Indep vars   = 1
 # Iterations   = 6
```

T=60°C

POLYMATH Results

POLYMATH Report 03-20-2010

Nonlinear regression (L-M)

Model: t = (8.16e-4^(1-0.60)-CA^(1-0.60))/(k*(1-0.60))

Variable	Ini guess	Value	95% confidence
k	5.0E-06	1.094E-04	1.067E-05

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9315778
R^2adj = 0.9315778
Rmsd = 7.543201
Variance = 632.2209

General
Sample size = 10
Model vars = 1
Indep vars = 1
Iterations = 9

Concentrations as a function of time for T= 100°C

POLYMATH Results

Concentrations as a function of time 03-03-2010, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	300	300
Ca	8.16E-04	1.113E-05	8.16E-04	1.113E-05
T	371.15	371.15	371.15	371.15
k	0.0678638	0.0678638	0.0678638	0.0678638
Cao	8.16E-04	8.16E-04	8.16E-04	8.16E-04
a	0.582	0.582	0.582	0.582
Cbo	0.005015	0.005015	0.005015	0.005015

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(Ca)/d(t) = -k*Cbo*(Ca)^a

Explicit equations as entered by the user

[1] T = 371.15
[2] k = 3681.222*exp(-4046/T)
[3] Cao = 8.16E-04
[4] a = 0.582
[5] Cbo = 5.015e-3

Independent variable

variable name : t
initial value : 0
final value : 300

Precision

Step size guess. h = .000001
Truncation error tolerance. eps = .000001

General

number of differential equations: 1
number of explicit equations: 5
Data file: C:\Documents and Settings\Owner\Desktop\PSM II\kinetic modeling\s.pol

Concentrations as a function of time for T= 70ºC

POLYMATH Results

Concentrations as a function of time 03-03-2010, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	380	380
Ca	8.16E-04	2.091E-04	8.16E-04	2.091E-04
T	343.15	343.15	343.15	343.15
k	0.0278823	0.0278823	0.0278823	0.0278823
Cao	8.16E-04	8.16E-04	8.16E-04	8.16E-04
a	0.582	0.582	0.582	0.582
Cbo	0.005015	0.005015	0.005015	0.005015

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -k*Cbo*(Ca)^a

Explicit equations as entered by the user
[1] T = 343.15
[2] k = 3681.222*exp(-4046/T)
[3] Cao = 8.16E-04
[4] a = 0.582
[5] Cbo = 5.015e-3

Independent variable
variable name : t
initial value : 0
final value : 380

Precision
Step size guess. h = .000001
Truncation error tolerance. eps = .000001

General
number of differential equations: 1
number of explicit equations: 5
Data file: C:\Documents and Settings\Owner\Desktop\PSM II\kinetic modeling\s.pol

Concentrations as a function of time for T= 60ºC

POLYMATH Results

Concentrations as a function of time 03-03-2010, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	300	300
Ca	8.16E-04	4.225E-04	8.16E-04	4.225E-04
T	333.15	333.15	333.15	333.15
k	0.0195715	0.0195715	0.0195715	0.0195715
Cao	8.16E-04	8.16E-04	8.16E-04	8.16E-04
a	0.582	0.582	0.582	0.582
Cbo	0.005015	0.005015	0.005015	0.005015

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -k*Cbo*(Ca)^a

Explicit equations as entered by the user
[1] T = 333.15
[2] k = 3681.222*exp(-4046/T)
[3] Cao = 8.16E-04
[4] a = 0.582
[5] Cbo = 5.015e-3

Independent variable
variable name : t
initial value : 0
final value : 300

Precision
Step size guess. h = .000001
Truncation error tolerance. eps = .000001

General
number of differential equations: 1
number of explicit equations: 5
Data file: C:\Documents and Settings\Owner\Desktop\PSM II\kinetic modeling\s.pol