BIODIESEL PRODUCTION FROM RUBBER SEED OIL USING ACTIVATED CLINKER AS CATALYST

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Biotechnology).

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STUDENT’S DECLARATION

I declare that this thesis entitled “Biodiesel Production from Rubber Seed Oil Using Activated Clinker as 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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Dedicated to:

Supportive family
Especially Mom Daljit Kaur
Faithful friends
Supervisor Dr Jolius Gimbun

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ABSTRACT

This study uses clinker from the cement industry as a catalyst for transesterification of rubber seed oil to biodiesel. Clinker is nodules that are obtained from sintering limestone and aluminosilicate. Accordingly, there is a need to overcome depletion of fossil fuel, fluctuating price of edible oil which is used as biodiesel feedstock and expensive noble metals. The immediate objective of this research project is to synthesize catalyst from clinker for biodiesel production and to elucidate the mechanism of catalyst activation of the cement waste. Rubber seeds were collected, dried and shelled from the kernels. Microwave extraction was used to extract the rubber seed oil using hexane as the extraction solvent. Density of rubber seed oil was determined using density meter, calorific value using bomb calorimeter, acid test using potentiometer, FFA content and fatty acid methyl ester content using gas chromatography; all the test complied with ASTM D1480, D240, D664 and D 1983 for GC. Clinker collected from the conveyer belt was crushed using the jaw crusher to obtain clinker size of below 5mm. Crushed clinker was then grinded using mortar and pestle and was passed through 200 μm sieve. Mineral composition was analysed using XRF and surface area of clinker was found using Blaine apparatus. SEM analysis was done to study the activation and concluded the optimum activation parameter morphologically for transesterification. Clinker was activated at 64.7 °C under reflux for 1 hour with catalyst methanol ratio of 1:400 using catalyst loading determined through acid test of rubber seed oil with constant stirring at 400 rpm. Reaction was done under reflux at methanol boiling point, 60 ± 0.5 °C with constant stirring for 1 hour. After reaction, the reaction mixture was allowed to settle in a separating funnel overnight. The top layer (fatty acid methyl ester) was pipette out followed by the second layer (glycerol). The top layer was washed 3 times with distilled water to remove methanol and impurities. GC analysis was done for fatty acid methyl ester. Clinker was found to contain 66.61% of CaO and 2.7% free lime. Surface area is found to be 0.56 m^2/g and acid number of FFA is 1.7952 mg KOH/g. Calorific value and density of FAME is 38.87 mJ/kg and 0.8548 g/cm^3. The entire test done to date supports the use of clinker as a novel catalyst to produce biodiesel.

ABSTRAK

Kajian ini menggunakan klinker daripada industri simen sebagai pemangkin dalam proses pembuatan biodiesel daripada minyak biji getah. Klinker adalah nodul yang diperolehi daripada pensinteran batu kapur dan aluminosilikat. Sehubungan dengan itu, adalah perlu untuk mengatasi masalah sumber bahan api fosil sedang menyusut serta harga minnyak masak yang digunakan sebagai bahan mentah biodiesel dan logam yang semakin meningkat. Objektif projek penyelidikan ini adalah untuk mensintesis pemangkin daripada klinker bagi pengeluaran biodiesel dan untuk menjelaskan mekanisme pengaktifan pemangkin sisa simen. Biji getah telah dikumpulkan, dikeringkan dan dibuang kulit dari biji. Pengekstrakan gelombang mikro digunakan untuk mengekstrak minyak biji getah menggunakan heksana sebagai pelarut pengeskstrakan. Ketumpatan minyak biji getah adalah ditentukan dengan menggunakan meter ketumpatan, nilai kalori menggunakan meter kalori bom, ujian asid menggunakan potensiometer, kandungan FFA dan kandungan metil ester asid lemak dengan menggunakan kromatografi gas; semua ujian mematuhi ASTM D1480, D240, D664 dan D1983 untuk GC . Klinker yang dikumpul dari "conveyer belt" dihancurkan menggunakan penghancur rahang untuk mendapatkan saiz klinker di bawah 5mm. Klinker yang telah dihancurkan kemudiannya dikisar menggunakan lesung dan alu dan telah dilalukan melalui ayak 200 µm. Komposisi mineral dianalisa menggunakan XRF dan permukaan kawasan klinker didapati menggunakan radas Blaine. SEM analisis telah dilakukan untuk mengkaji pengaktifan dan untuk membuat kesimpulan parameter pengaktifan optimum morfologi untuk transesterification. Klinker telah diaktifkan pada 64,7 °C di bawah refluks selama 1 jam dengan nisbah metanol pemangkin 1:400 pemangkin loading yang ditentukan melalui ujian asid minyak biji getah dengan mengacau larutan pada kadar tetap; 400 rpm. Tindak balas telah dilakukan di bawah refluks pada suhu 60 ± 0.5 °C dengan mengacau berterusan selama 1 jam. Selepas tindak balas, campuran tindak balas dibiarkan semalama. Lapisan atas (metil ester asid lemak) dipipet keluar diikuti oleh lapisan kedua (gliserol). Lapisan atas dicuci 3 kali dengan air suling untuk mengeluarkan sisa metanol berlebihan dan kotoran. Analisis GC telah dilakukan untuk menentukan komposisi metil ester asid lemak. Klinker didapati mengandungi 66,61 % CaO dan 2.7 % kapur. Luas permukaan didapati 0.56 m^2/g dan nombor asid FFA 1.7952 mg KOH/g. Nilai kalori dan ketumpatan FAME adalah 38.87 mJ/kg dan 0.8548 g/cm3 masing-masing. Keseluruhan ujian yang dilakukan setakat ini menyokong penggunaan klinker sebagai pemangkin novel untuk menghasilkan biodiesel.

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LIST OF SYMBOLS

%	Percentage
°C	Degree celsius
min	Minute
µm	Micrometer
vol. %	Volume percentage
cm	Centimeter
W	Watt
g	gram
m	Metre
s	Second
ha/yr	hectare per year
ha	hectare
K	Kelvin
mm^2/s	milimeter square per second
kJ/kg	Kilo Joule per kilogram
meq/kg	miliequivalent per litre
wt %	weight per cent
ml	millilitre
ml/min	millilitre per minute

LIST OF ABBREVIATIONS

FAME	Fatty Acid Methyl Ester
FFA	Free Fatty acid
TG	Triglycerides
RSO	Rubber Seed Oil
CLK	Clinker
ASTM	American Society for Testing and Material
LHV	Lower Heating Value
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The current motivation towards the production of biodiesel is the conservation of fossil fuels as well as concerns over environmental problems. Considerable attention and effort has been given in producing alternative renewable energy like biodiesel which is also known as Fatty Acid Methyl Ester (FAME) (Canakci, 2006). FAME is an alternative biofuel produced through transesterification of triglycerides (TGs) or the esterification of Free Fatty Acids (FFAs) with methanol (Meher et al., 2006). Besides that, biodiesel possesses all the favourable characteristics of diesel and is renewable, biodegradable, non toxic and ‘carbon neutral’ since no net amount of carbon is released to the atmosphere.

Biodiesel also has cetane number of 100 which is 60% more than in diesel. This parameter shows that biodiesel will allow cold starts and less idle noise (Lotero et al., 2005). According to Ramadhas et al. (2004), biodiesel have no sulphur content, no storage difficulties and have good lubricating properties According to Dorado and Loperz (2006), vegetable oils and fats are the main feedstock for biodiesel and an economical supply that is sustainable is a crucial factor.

Ramadhas et al. (2004) further elaborated that vegetable oils are a promising alternative to fossil fuel as they are renewable and nature friendly because they help to decrease carbon content in atmosphere. Many researchers used edible oils for example sunflower and corn to produce biodiesel but the fluctuating prices of edible oils and increasing demands for nutritional needs have made rubber seed oil to be the raw material of choice (Yusup and Khan, 2010). Biodiesel production from edible vegetable oils and animal fats as feedstock creates a big concern over the competition in the food supply. In order to overcome these issues, there is a dire need to produce biodiesel using second generation vegetable oil and the use of catalyst that reduces energy requirement in transesterification as well as cost effective.

Current biodiesel production technology uses noble metal as catalyst. Besides that, it is cannot be recycled and production cost is high due to it. Separation also becomes another problem as purification of biodiesel becomes difficult.

This research is about the production of biodiesel from rubber seed oil (RSO) using activated cement clinker as the catalyst in transesterification process.

1.2 STATEMENT OF PROBLEMS

According to Issanyakul and Dalai (2010), first generation biodiesel was produced from edible oils and the second generation biodiesel was produced from non-edible oils. The use of edible oil is seen as not being feasible according to their research. Following are the problems that have been identified with biodiesel production previously.

1.2.1 Depletion of Fossil Fuel and Degradation of Environmental Quality

Major part of energy source comes from the non-renewable fossil fuel which also pollutes the environment significantly (Sharma and Singh, 2010). Besides that, price of fossil fuel is also rocketing as the demand is higher than supply itself.

1.2.2 Fluctuating Prices of Edible Oils and Expensive Noble Metal

The use of edible oils is no longer feasible as demand for nutrition predominate the need for energy. Their availability is a concern thus prices of edible oils increases (Sarin et al., 2009). Lin et al. (2009) has stated that noble metal catalyst used in transesterification is expensive. Most of the catalyst used is non-recyclable. This causes the price of biodiesel to increase.

1.3 RESEARCH OBJECTIVES

The sole objective of this research is to produce biodiesel from rubber seed oil using catalyst derived from cement industry. Activation and characterisation of cement clinker (CLK) will be done to test its suitability as heterogeneous catalyst.

1.4 SCOPE OF STUDY

The following are the scope of study of this research:

1.4.1 Extraction of Rubber Seed Oil (RSO) From Kernels Using Soxhlet Extraction and Microwave Extraction.

1.4.2 Characterisation of Extracted RSO Using ASTM Standards.

1.4.3 Activation and Characterisation of Cement Clinker.

1.4.4 Transesterification of RSO with Activated Cement Clinker to Produce Methyl Ester (Biodiesel). Optimum Catalyst Loading Will Be Tested As Part Of Kinetic Studies.

1.4.5 Biodiesel Analysis Using ASTM Standards And Comparing With Values Of Other Feedstock.

1.5 EXPECTED OUTCOMES

It is expected that by using activated cement clinker as catalyst, a high yield of FAME can be obtained within the shortest period of transesterification reaction time of 1 hour with an acceptable biodiesel characterisation within the specifications of ASTM D 6751 for B100.

1.6 SIGNIFICANCE OF STUDY

Below are the significance of this research in terms of its novelty, applicability and commercialization.

1.6.1 Novelty of Biodiesel Production from Rubber Seed Oil

First generation feedstock used edible vegetable oil. Using crops for energy and food compete with each other in many ways (agricultural land, skilled labours, water, fertilizers, etc.). Using second generation feedstock which is non- edible vegetable oil will be more feasible. Besides that, activated cement clinker will be used as a catalyst instead of the expensive noble metals.

1.6.2 Applicability of This Study

Use of rubber seeds and cement clinker is a great opportunity to convert waste to wealth and recycling of catalyst for cost efficient biodiesel production.

1.6.3 Commercialisation

According to statistics done by KDPN HEP, annual consumption of diesel in Malaysia in year 2010 was 11.655 billion litres. Annual revenue of RM 340.082 billion can be generated if biodiesel from rubber seed oil is sold at RM 2.581 per litre (Biofuel Database in East Asia), the current price in 2011 for fossil diesel.

1.7 CONCLUSION

It is hoped that biodiesel can be produced from rubber seed oil using activated clinker as the catalyst for transesterification using the scope outlines and the amount of FFA in crude oil can be reduced.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This section will discuss the reviews on biodiesel production from rubber seed oil using activated clinker as catalyst. This review will be divided into; (a) depletion of fossil fuel and introduction to biodiesel, (b) types of feedstock available and selection of feedstock, (c) types of catalyst and selection of catalyst and (d) methods to produce biodiesel.

2.2 Depletion of Fossil Fuel and Introduction to Biodiesel

As a result of the birth of industrial revolution in the late 18th and early 19th, energy has become a crucial reason for human to protect economic growth and maintain standard of living. The extension of industrial revolution in Europe had been largely contributed by the abundant availability and accessibility of coal as the primary source of energy. On the other hand, the arrival of automobiles, airplanes and electricity had been made possible by the energy use of petroleum in the 20th century. Marked to this date, energy has been continuously obtained from conventional sources (fossil fuels).

Currently, we are facing problems like depletion of fossil fuel, increasing demands for diesels and uncertainty in the availability of fossil fuel (Singh and Singh, 2010). There is excess use of fossil fuel and it is predicted that in another 80 years, mankind will face huge problems. Fossil fuels take millions of year to form from bacteria activities from beneath the sea levels.

According to Shay (1993), Rudolf Diesel first tested the use of vegetable oil in particular, peanut oil as fuel for his engine about 120 years ago. The usage of this biofuel continued until 1920s before petroleum-derived diesel almost completely vanished vegetable oils in the market because of its lower price, higher availability and government subsidies.

Biodiesel is an initiative alternative source of energy that is being produced to overcome fossil fuel depletion. This can be seen from the effort that had been started over a century ago. Alternative fuel has been accepted as early 1982 by holding the first international conference on plant and vegetable oils as fuels (Singh and Singh, 2010). Even in Kyoto Protocol, the use of biodiesel throughout the world has been advised. The European Community in 1991 has proposed a tax reduction of 90% for the use of biofuels including biodiesel (Haque et al., 2009).

Biodiesel is beneficial as it is renewable, biodegradable, non-toxic and aromatic. It is also sulphur free and has potential in reducing levels of pollutants and probable carcinogens (Martini and Shell, 1998). Due to having better properties than that of petroleum diesel itself, it can be concluded that the search for biodiesel is indeed beneficial to mankind as it has many advantages as a substituent.

2.3 Types of Feedstock Available and Selection of Feedstock

There are various types of suitable raw materials for biodiesel production. There are many types of vegetable oil and animal fats that can be used as raw materials in biodiesel production (Lee et al., 1995). The feedstock for biodiesel can vary from one country to another country depending on their geographical locations and agricultural trend (Bryan, 2009). Most of the raw materials used are first generation feedstocks which are edible. Edible feedstock should not be used as it will not be cost effective and it is not feasible to be used in a larger scale. If this issue is viewed in countries with large population like India and China, there is a large gap between the demand for fuel and supply provided (Singh and Singh, 2010). There will be fight over for sustainability and food for fuel production. In India, only plants that are non-edible which can produce oil in an acceptable quantity and that can be grown on large scale on non- cropped marginal and waste lands can be used. A list of biodiesel feedstock in the form of vegetable oils, non-edible oils, animal fats and some other biomass are listed in Table 2.1.

Table 2.1: List of biodiesel feedstock

Vegetable oils	Non-edible oils	Animal fats	Other sources
Soybeans	Almond	Lard	Bacteria
Rapeseed	*Abutilon muticum*	Tallow	Algae
Canola	Andiroba	Poultry fat	Fungi
Safflower	Babassu	Fish oil	Micro algae
Barley	*Brassica carinata*		Tapenes
Coconut	*B. napus*		Latexes
Copra	Camelina		Cooking oil
Cotton seed	Cumaru		(Yellow grease)
Groundnut	*Cynara*		Microalgae
Oat	*carduncului*s		(Chlorellavulgaris)
Rice	Jatrophacurcas		
Sorghum	*Jatropha nana*		
Wheat	Jojoba oil		
Winter rapeseed oil	Pongamiaglabra		
	Laurel		
	Lesquerellafendleri		
	Mahua		
	Piqui		
	Palm		
	Karang		
	Tobacco seed		
	Rubber plant		
	Rice bran		
	Sesame		
	Salmon oil		

Source: Singh and Singh (2010)

As seen in Table 2.1, there are many concerns regarding the use of vegetable oils in terms of its applicability and also the cost of biodiesel. The price of vegetable oil is high and therefore using it will not be cost effective (Singh and Singh, 2009). Selecting the best feedstock is important to make sure of low biodiesel production cost. Feedstock supply and price alone contributes to 75% of the overall production (Meng et al., 2009). To ensure that biodiesel remain comparable to petroleum-derived diesel, feedstock should be accessible at the lowest price possible and abundantly available. Using wheat and rice as biodiesel feedstock will definitely not be feasible as it the staple food in most countries. Ramadhas et al. (2005) revealed that vegetable oils have no sulphur content, offer no storage difficulty, have excellent lubricating properties, absorb more carbon dioxide and will definitely help to reduce carbon dioxide content in atmosphere.

Of all the available feedstock, Yusup and Khan (2010) suggest that rubber seeds are underutilised and have no major application in industry. Rubber seeds are also easily available in Malaysia (Yusup and Khan, 2010). Based on research done by Eka et al. (2010), there were estimated acreage of 1, 229, 940 hectares of rubber plantation in 2007. An estimated average of 1000 kg seeds per ha/ yr are produced. Rubber trees cover more than 1.2 million ha all over the country (Malaysian Rubber Board Statistics, 2009). Each hectare can give approximately 150 kg of seeds. Rubber seed kernels (50-60 % of seed) contain 40-50% of brown colour oil (Ramadhas et al., 2005). Ramadhas et al. further characterised rubber seeds stating that they are ellipsoidal, variable in size, 2.5-3 cm long, mottled brown, lustrous, weighing 2-4 g each.

2.4 Rubber Seed Oil and Fuel Characterisation

The establishment and commercialisation of biodiesel in many countries around the world has triggered the development of standards to ensure and promise high quality of product and user confidence. Two of the widely used biodiesel standards are ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN14214. Biodiesel is characterised by determining its physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. In conclusion, biodiesel compares well to petroleum-based diesel

The benefits offered by biodiesel outweigh that of diesel itself. According to Demirbas (2009), “The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulphur and aromatic content, higher cetane number and higher biodegradability”. The obvious disadvantages of biodiesel as diesel fuel on the other hand are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide emission, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear as stated by Demirbas (2008).

There are more safety benefits offered by biodiesel compared to diesel fuel as it is much less combustible, with a flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel (Demirbas and Balat, 2006). Biodiesel has a higher cetane number (around 50) than diesel fuel (Balat and Balat, 2008). Cetane number is used as indicator to determine diesel fuel quality, especially the ignition quality. It is to measure the readiness of the fuel to auto-ignite when injected into the engine. Ignition quality is determined by the structure of the fatty acid methyl ester (FAME) component (Bamgboye and Hansel, 2008). Viscosity is a very vital property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has viscosity which is close to that of diesel fuels. High viscosity causes poorer atomization of the fuel spray and less accurate operation of the fuel injectors (Balat, 2008). Due to presence of electronegative element oxygen, biodiesel is slightly more polar than diesel fuel as a result viscosity of biodiesel is higher than diesel fuel. Presence of elemental oxygen lowers the heating value of biodiesel when compared the diesel fuel (Kulkarni et al., 2008). The lower heating value (LHV) is the most common value used for engine applications. It is used as an indicator of the energy content of the fuel. Biodiesel generally has a LHV that is 12 % less than because of its environmental benefits and the fact that it is made from renewable resources.

The properties biodiesel in comparison with standard biodiesel and diesel (Table 2.2) can be observed.

Table 2.2: Shows properties of rubber seed oil in comparison with diesel

Property	**Test procedures**	**Rubber seed oil**	**Diesel**
Specific gravity	ASTM D4052	0.91	0.835
Viscosity (mm^2/s)	ASTM D445	76.4	7.50
Flash point (°C)	ASTM D93	198	50
Calorific value (kJ/kg)	ASTM D240	37 500	42 250
Iodine value	-	135.3	38.3
Acid value	ASTM D974	53.0	0.062

Source: Ramadhas et al. (2005)

If seen in the above table, the acid value of crude rubber seed oil is critically high if compared to diesel's acid value. Khan et al. (2010) has clearly stated using crude non-edible oils and fats contribute to high free fatty acid (FFA) content.

For instance, the rubber seed oil extracted in Jose et al. (2011)'s study shows that it contains 35 mg KOH/g, which is equivalent to 17.5 % FFA. High FFA contents prevent single step transesterification using base catalyst because saponification takes place and forms soap. This will harden the separation process of ester and glycerol (Ikwuagwu et al., 2000). Yusup and Khan (2010) reported that using refined and bleached rubber seed oil before running the experiment lowers the acid value but at the same time they agreed that refining will add cost to the process. Jose et al. (2011) also related high FFA with high viscosity of oil. Besides that, acid esterification is also widely used to treat high fatty acid crude rubber seed oil (Khan et al., 2010).

Table 2.3: Physiochemical properties of crude oil and refined (bleached) rubber seed oil

Analysis	**Crude rubber seed oil**	**Refined rubber seed oil**
Physical state at 30 °C	Liquid	Liquid
Colour	Golden yellow	Golden yellow
Specific gravity at 30 °C	0.922	0.918
Refractive index at 40 °C	1.4654	1.4650
Viscosity (cSt) at 30 °C	41.24	37.85
Smoke point (°C)	245	244
Flash point (°C)	294	290
Fire point (°C)	345	345
Acid value	4.0	1.0
Free fatty acid (as oleic)	2.0	0.5
Peroxide value (meq/kg)	2.5	1.0
Iodine value	142.6	142.6
Saponification value	194.0	185.8
Unsaponifiable matter	1.18	0.16

Source: Ikwuagwu et al. (2000)

Table 2.4: Yields of ester-fuel (weight per cent)

	% Yield of ester at 30 °C	**% Yield of glycerol**
Crude oil	76.64	13.98
Refined (bleached) oil	84.46	8.79

Source: Ikwuagwu et al. (2000)

It can be seen obviously that after refining the crude oil, the yield of ester increases. Therefore, to get a higher product, crude oil need to be refined to bring down acid value, eliminate the chances of saponification and increase product yield. Added cost for refining is inevitable but it will be cut off with the product sales.

Table 2.5: Properties biodiesel in comparison with standard biodiesel and diesel

Property	**Test procedure**	**Biodiesel-Standard ASTM D6751-02**	**Rubber seed oil-biodiesel**	**Diesel**
Specific gravity at 30 °C	ASTM D4052	0.87-0.90	0.837	0.839
Kinematic Viscosity at 40 °C (mm^2/s)	ASTM D445	1.9-6.0	3.12	3.18
Heating value (kJ/kg)	ASTM D240	-	38.20	42
Flash point (°C)	ASTM D93	Max 130	128	68
Cloud point (°C)	ASTM D2500	-3 to 12	5	17
Pour point (°C)	ASTM D97	-1.5 to 10	-7	-20
Carbon residue (%)	-	<0.3	0.14	0.17

Source: Jose et al. (2011)

The marketability of vegetable oil depends on its fatty acids and the convenience to be modified or altered with the use of other chemicals (Pryde and Rothfus, 1989). The content of fatty acids in rubber seed oil is as follows; 17-20 % saturated fatty acids (myristic, palmitic, stearic, arachidic and behenic) and 77-82 % unsaturated fatty acids (palmitoleic, oleic, linoleic, linolenic and arachidoleic) (Hardjosuwito and Hoesnan, 1978).

2.5 Production of Biodiesel

In section 2.4, we have seen that Jose et al. (2011) has related high FFA with high viscosity of oil. His finding shows that there are several ways to bring down viscosity of oil; emulsification, pyrolysis and transesterification etc.

Pyrolysis is a thermochemical conversion technology used to produce energy from biomass. It involves the heating of organic materials in the absence of reagents, especially oxygen, to achieve decomposition (Sonntag, 1979). Fukuda et al. (2001) conducted an experiment using pyrolysis which resulted in products with low viscosity, high cetane number, accepted amounts of sulphur, water and sediments, accepted corrosion copper corrosion values but then was unacceptable in terms of their ash contents, carbon residues and pour points.

Comparably, micro-emulsification of vegetable oil done by Fukuda et al. lowered the viscosity of vegetable oil but resulted in irregular injector needle sticking, heavy carbon deposits and incomplete burning during 2000 hour of laboratory screening endurance test.

Tansesterification on the other hand is a chemical reaction between triglyceride and alcohol in or without the presence of a catalyst. Catalyst can fall under acid catalyst, alkaline catalyst or even bio-catalyst which will be further discussed in Section 2.6. This process consists of a sequence of three consecutive reversible reactions where triglycerides are converted to diglycerides, and diglycerides to monoglycerides then succeeded by the conversion of monoglycerides to glycerol. In each conversion step, an ester is produced which makes the production of a total of three molecules of ester from one molecule of triglyceride (Sharma and Singh, 2007). Of all these methods, transesterification is found to be the best because glycerol as the by-product has commercial value (Ramadhas et al., 2005).

For alcohol needed, it is usually three moles of alcohols in accordance to every mole of triglyceride but for maximum ester production, higher molar ratio is often employed. This is also dependent on the type of feedstock used, amount of catalyst employed and reaction temperature set. Most commonly used alcohols are methanol, ethanol, propanol and butanol but the selection is usually done on the basis of the most cost efficient material. Methanol is generally preferred due to its low cost (Ramadhas et al., 2004).

In alkali catalysed transesterification, three reaction mechanism steps are used. The first step is to form an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (Methoxide ion) to form a tetrahedral intermediate which then reacts with an alcohol (methanol) to regenerate the anion of alcohol (methoxide ion). In the final step, the rearrangement of tetrahedral intermediate will result in the formation of a fatty acid ester and a diglyceride. When alkaline catalyst is mixed with alcohol, the actual catalysts, alkoxide group is formed (Sridharan and Mathai, 1974). For an alkali catalysed transesterification, the glycerides and alcohol must be substantially anhydrous (Wright et al., 1944) because water makes the reaction partially change to saponification, which produces soap. In most cases where alkaline catalysts have been used in reaction, the FFAs (free fatty acids) were removed from the process stream as soap and considered waste. Waste greases typically contain from 10 to 25 % FFAs. This is far beyond the level that can be converted to biodiesel using an alkaline catalyst.

Acid catalyst transesterification on the other hand is an alternative process which uses acid catalyst for producing biodiesel. Research has shown that acid catalyst has more tolerance towards free fatty acids (Liu, 1994). Figure 2.3 shows the acid catalysed transesterication for a monoglyceride. This reaction can be extended to diglyceride and triglycerides as well. Protonation of carbonyl group of the ester leads to the carbocation in which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst. We can use acid alkali and biocatalyst in transesterification method. If more water and free fatty acids are in triglycerides, acid catalyst can be used (Keim, 1945). Transemethylation occur approximately 4000 times faster in the presence of an alkali catalyst than those catalysed by the same amount of acidic catalyst (Formo, 1954).

$$Triglycerides + ROH \xrightarrow{CATALYST} Diglycerides + R'COOR \tag{2.1}$$

$$Diglycerides + ROH \xrightarrow{CATALYST} Monoglycerides + R''COOR \tag{2.2}$$

$$Monoglycerides + ROH \xrightarrow{CATALYST} Glycerol + R'''COOR \tag{2.3}$$

Figure 2.1: Transesterification reaction

Source: Singh and Singh (2010)

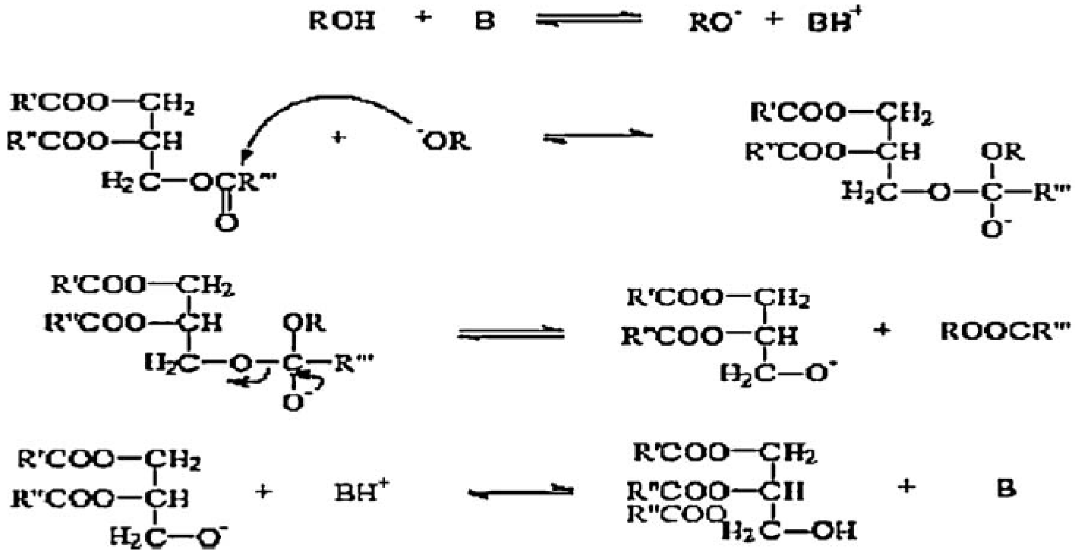


Figure 2.2: Mechanism of the alkali-catalysed transesterification of vegetable oils

Source: Singh and Singh (2010)

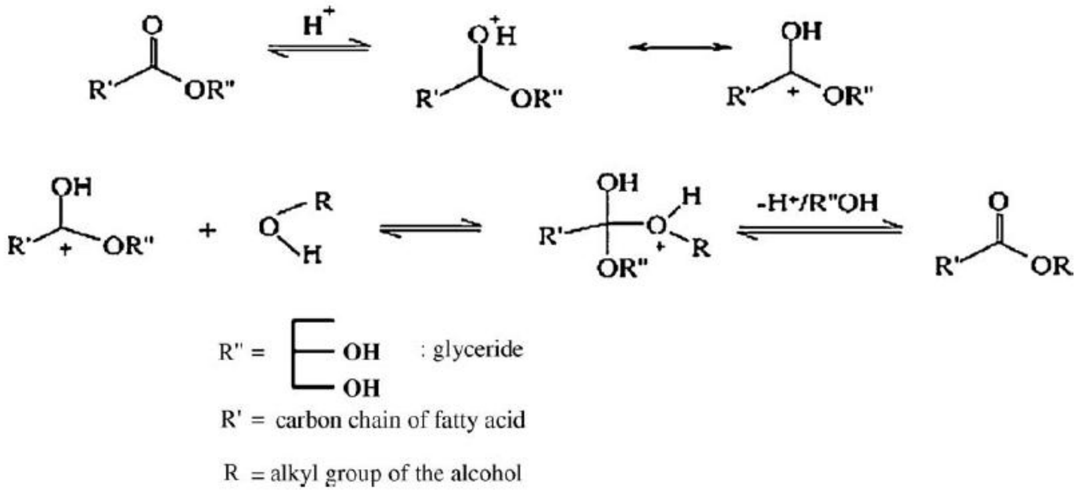


Figure 2.3: Mechanism of acid-catalysed transesterification

Source: Singh and Singh (2010)

Similarly, lipase catalyst transesterification is like alkali transesterification, only ratio of catalyst and solvent a stirring time different. Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones (Shimada et al., 1998).

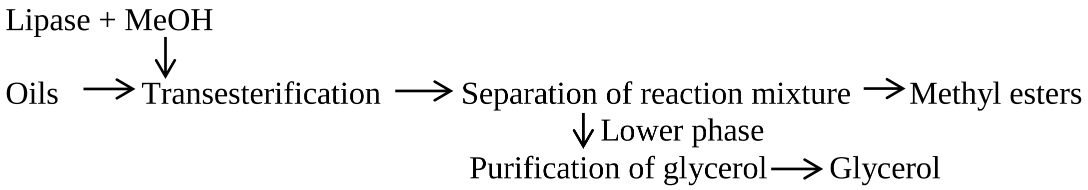


Figure 2.4: Flow diagram comparing biodiesel production using lipase catalyst

Source: Singh and Singh (2010)

2.6 Types of Available Catalyst and Catalyst Selection

As highlighted in the previous section, there are several categories of catalysts such as acid catalyst, alkaline catalyst and bio-catalyst. Catalyst itself can be divided into homogeneous catalyst and heterogeneous catalyst. Heterogeneous catalyst is a form of catalyst which is a different phase with the reactants (Rothenberg, n.d). In the case of biodiesel production, heterogeneous catalyst refers to the use of solid catalyst system. On the other hand, homogeneous catalyst refers to the phase of catalyst being the same as of the reactants. In the case of biodiesel production, the catalyst would be in liquid form. The type of catalyst used is also based on the choice of feedstock.

According to Shu et al. (2010), biodiesel production using waste oils should not utilise base-catalysed method because soap is produced from the reaction of FFA with base catalyst. Waste oils contains high amount of FFA. Therefore, the soap formed will consume the catalyst and causes the emulsification of FAME and glycerol which makes the FAME-glycerol mixture separation difficult (Georgogianni et al., 2008). In this scenario, the use of an acid catalyst would be a smart choice.

Nevertheless, there are also a few disadvantages of using acid catalyst which mostly are homogeneous. Problems such as corrosiveness, difficulty of separation from reaction medium and waste treatment arises due to the neutralisation of H_2SO_4. There are several types of heterogeneous catalyst that is being used for biodiesel production; zeolites, La/zeolite beta, MCM-41, silica-supported zirconium sulphate, Amberlyst-15 and Nafion (Shu et al., 2010).

It is vital to find the most suitable solid acid catalyst as heterogeneous acid catalyst is hydrophilic. Its activity decreases with the formation of water from the esterification of FFA. According to Nakajima et al. (2007), the acid catalysis over inorganic oxide solid takes place in the acidic hydroxyl groups (-OH) which acts as strong Bronsted acid sites. Therefore, the presence of –OH (hydration) will reduce the strength of acid.

As mentioned earlier, problems with waste occurs with the use of homogeneous catalyst due to several washing steps. This causes additional cost to the final product (Chawalit et al., 2010). This problem can be overcome with the use of heterogeneous catalyst as the separation and purification step is simplified and washing stages are omitted.

Currently, there is much interest in using calcium as catalyst in biodiesel production. If we take $CaCO_3$ for example; a natural rock, it has low activity and a high temperature of more than 200 °C which is required to obtain more than 95 % of oil conversion (Suppes et al., 2001). CaO is also being widely investigated by many researchers as a solid base catalyst for the transesterification. CaO has high basic strength of H = 26.5 which makes it to have high activity and long service lifetime (Liu et al., 2008). There are many sources of CaO such as $CaCO_3$-based materials including coral, sea shells and chalk.

The important thing that needs much attention with the use of CaO as catalyst is its modification through calcination and leaching in biodiesel (Huaping et al., 2006). When used as catalyst for biodiesel production from Jatropha oil, CaO resulted in 93% conversion and was reused up to three times with 92 % conversion. CaO used was treated with ammonium carbonate solution and calcination at 900 °C. What actually happens in calcination is that at high calcination temperature, calcium carbonate decomposes forming calcium methyloxide which acts as a surface intermediate in transesterification reaction.

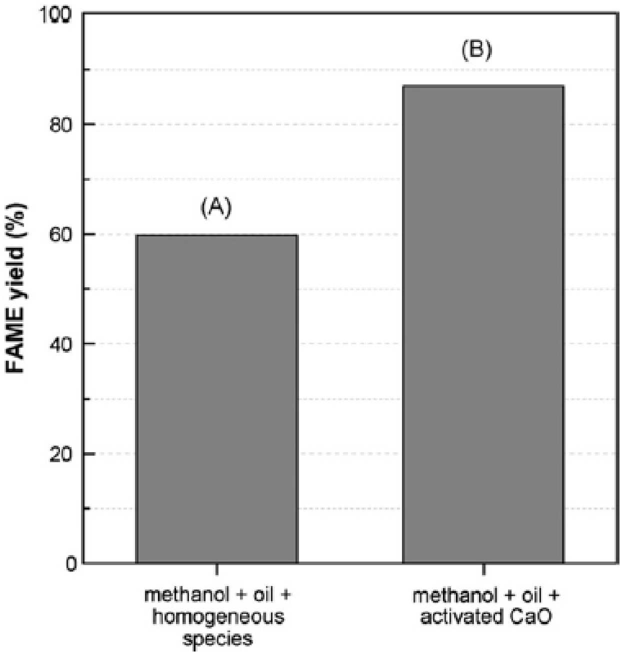


Figure 2.5: Yield of Fame obtained by using (a) homogeneous species created by contacting the methanol and the activated CaO for 2 h at 60 °C and (b) by using activated solid CaO

Source: Granados et al. (2007)

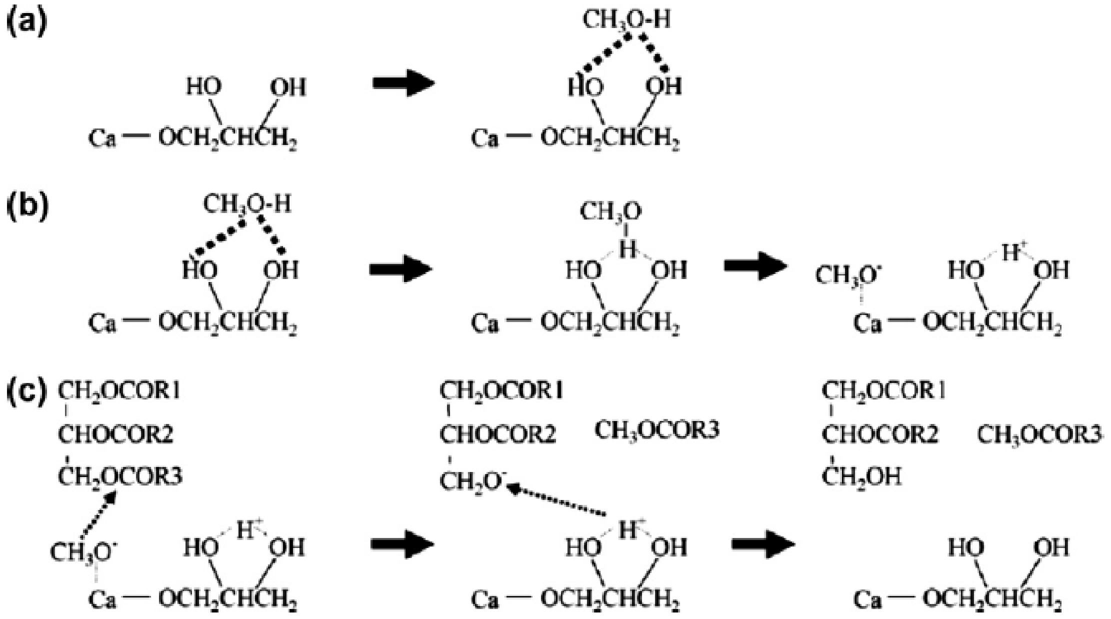
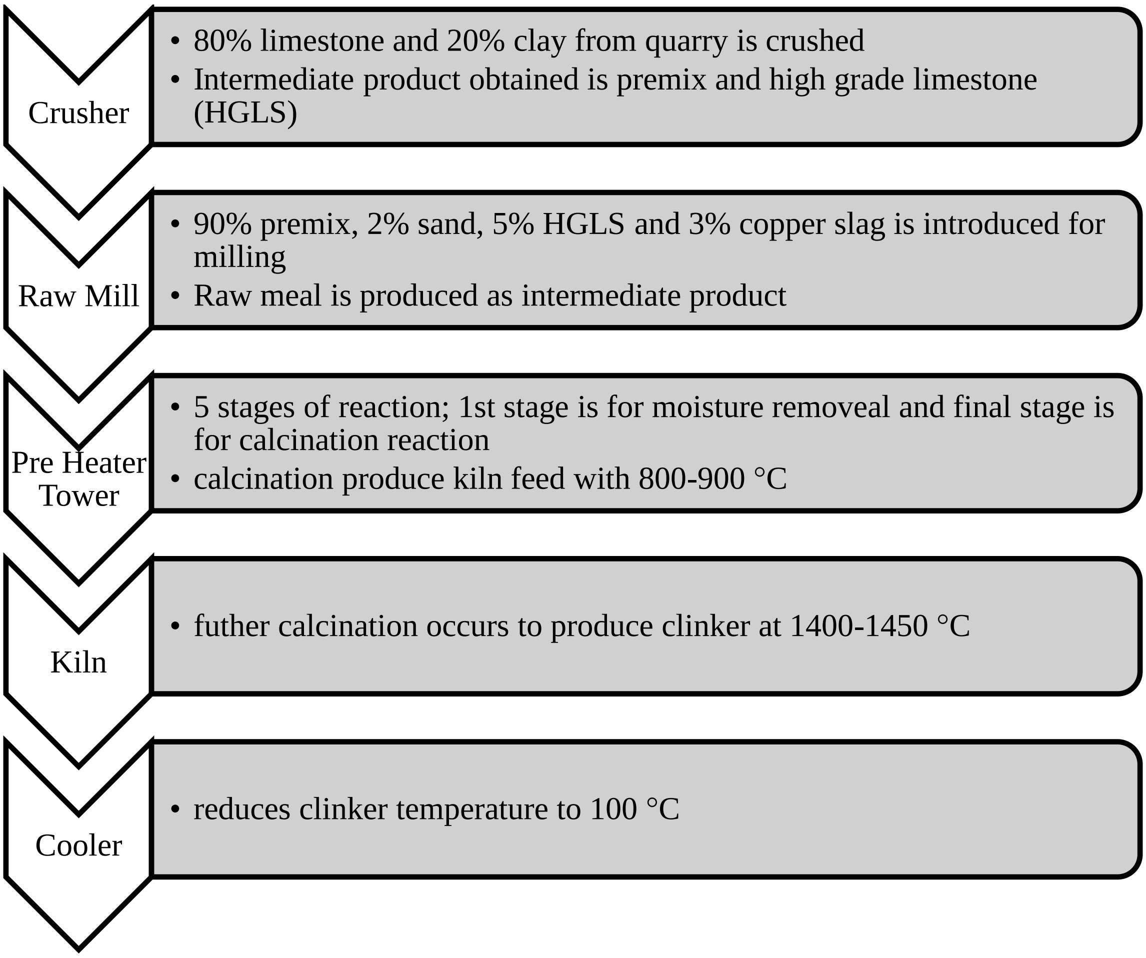


Figure 2.6: (a) Adsorption of methanol onto catalyst; (b) abstraction of proton by basic sites; and (c) nucleophilic reaction with methoxide anion followed by stabilization of the anion by proton

Source: Veljkovic et al. (2009)

In Figure 2.5, it can be seen that with the use of activated of CaO, the FAME yield increased by 47 %. In Figure 2.6 (a), the two OH groups favoured the adsorption of methanol-forming hydrogen bonds. In 2.6 (b), the OH groups enhanced the abstraction of protons.

In this research, the use of cement clinker as heterogeneous solid base catalyst is considered. Cement clinker is the major component in the cement industry used to produce the final product- cement after grinding with limestone and gypsum. Following are the steps involved in producing cement clinker as shown in Figure 2.7.



Crusher

- 80% limestone and 20% clay from quarry is crushed
- Intermediate product obtained is premix and high grade limestone (HGLS)

Raw Mill

- 90% premix, 2% sand, 5% HGLS and 3% copper slag is introduced for milling
- Raw meal is produced as intermediate product

Pre Heater Tower

- 5 stages of reaction; 1st stage is for moisture removeal and final stage is for calcination reaction
- calcination produce kiln feed with 800-900 °C

Kiln

- futher calcination occurs to produce clinker at 1400-1450 °C

Cooler

- reduces clinker temperature to 100 °C

Figure 2.7: Process manufacturing of cement clinker

The focus here is on clinkering to observe the chemical reaction that takes place in calcination. Calcination reaction is the decarbonation of the lime to become free CaO and release CO_2. There are four zones in the kiln which is about 60 m long, each reaction at different reaction time and temperature.

(a) In Zone 1, reaction occurs from time 0 min to 35 min at reaction temperature of 800 to 1100 °C. In this zone, decarbonation occurs in which $3CaO.Al_2O_3$ is formed at above 900 °C. Melting of fluxing compounds Al_2O_3 and Fe_2O_3 also happens.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2 \tag{2.4}$$

(b) In Zone 2, reaction occurs from time 35 min to 40 min at reaction temperature of 1100 to 1300 °C. In this zone, exothermic reactions and the formation of secondary silicate phases takes place as follow:

$$2CaO + SiO_2 \xrightarrow{heat} 2CaO.SiO_2 \tag{2.5}$$

(c) In Zone 3, reaction occurs from time 40 min to 45 min at reaction temperature of 1300 to 1450 to 1300 °C. In this zone, sintering and reaction within the melt to form ternary silicates and tetracalcium aluminoferrates as follows:

$$2CaO.SiO_2 + CaO \xrightarrow{heat+time} 3CaO.SiO_2 \tag{2.6}$$

$$3CaO.Al_2O_3 + CaO + Fe_2O_3 \xrightarrow{yields} 4CaO.Al_2O_3.Fe_2O_3 \tag{2.7}$$

(d) In Zone 4, reaction occurs from time 50 min to 60 min at reaction temperature of 1300 to 1000 °C. In this zone, cooling and crystallisation of the various mineral phases formed in the kiln (Bogue and Herman, 1955).

Figure 2.8: Cement clinker after cooling

The following Table 2.6 shows the summary of chemical reaction from the pre heater tower to kiln. Alite, Ca_3SiO_5 in terms of its oxides is $3CaO.SiO_2$. The CaO term is shortened to C and the SiO_2 to S. The compound thus becomes C_3S. Belite, Ca_2SiO_4 is $2CaO.SiO_2$, which is shortened to C_2S. Tricalcium aluminate, $Ca_3Al_2O_6$ is $3CaO.Al_2O_3$. The Al_2O_3 term is shortened to A and the compound becomes C_3A. Tetracalcium aluminoferrite, $2(Ca_2AlFeO_5)$ is $4CaO.Al_2O_3.Fe_2O_3$. Fe_2O_3 is shortened to F and the compound becomes C_4AF.

Table 2.6: Chemical Transformation in the Thermal Treatment of Portland Cement Raw Meal (Principle Reaction in Clinker Burning)

Temperature (°C)	**Process**	**Chemical Transformation**
< 200	Escape of free water (drying).	
100 – 400	Escape of adsorbed water	
400 – 750	Decomposition of clay, e.g. with formation of metakaoline.	$Al_4(OH)_8Si_4O_{10} \rightarrow 2(Al_2O_3.2SiO_2) + 4H_2O$
600 – 900	Decomposition of metakaoline and other compounds with formation of a reactive oxide mixture.	$Al_2O_3.2SiO_2 \rightarrow Al_2O_3 + 2SiO_2$
600 – 1000	Decomposition of limestone with formation of CS and CA.	$CaCO_3 \rightarrow CaO + CO_2$ $3CaO + 2SiO_2 + Al_2O_3 \rightarrow 2(CaO.SiO_2) + CaO.Al_2O_3$
800 – 1300	Uptake of lime by CS and CA with formation of C_4AF.	$CS + C \rightarrow C_2S$ $CA + 2C \rightarrow C_3A$ $CA + 3C + F \rightarrow C_4AF$
1250 – 1450	Further uptake of lime by C_2S.	$C_2S + C \rightarrow C_3S$

Source: Lea (1970)

From the chemical reaction that occurs, it can be concluded that cement clinker contains high percentage of CaO. In Table 2.7, the chemical composition in clinker can be seen.

Table 2.7: Typical clinker analysis (oxide weight %)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Total
21.5	5.2	2.8	66.6	1.0	0.6	0.2	1.0	98.9

Source: WHD Microanalysis Consultants (2005)

In this analysis, free lime consists about 1.0 %. The balance is typically due to small amounts of oxides of titanium, manganese, phosphorus and chromium. Cement clinker can be used to convert feedstock acids or esters to biodiesel. It is preferred due to its advantages. Firstly, it is insoluble heterogeneous catalyst that can easily be separated without washing or neutralisation. Therefore, it is recyclable and can be used up to 20 times after activation with methanol. Activation procedure of clinker is of low cost. Besides that, catalyst material is stable and is highly active in producing biodiesel. And finally, catalyst with reduced reactivity after numerous uses can be regenerated through calcinations (Lin et al., 2011).

Lin et al. further stated that, transesterification with KOH need precise neutralisation process with strong acids and extensive washes with water to remove the resulting salt. Glycerol formed must be separated from the salt using vacuum distillation (because glycerol’s boiling point is high). This problem will not be faced by using clinker as it traps the glycerol and other impurities. No additional water washing step is required as well.

At present catalyst used cannot be recycled. Besides, high solubility of catalysts adds cost. There is need for an efficient, inexpensive and environmentally friendly catalyst and clinker is found to fulfil all this. Clinker contains calcium oxide which is basic and can serve as a catalyst for transesterification (Lin et al., 2011).

Lin and associates have very much discussed their findings on ways to activate the catalyst. One of the suggested methods is by suspending catalyst in alcohol before adding it into feedstock accompanying by stirring for 20 to 30 min. The second method suggested is by impregnating the catalyst in methanol without stirring but with agitation for example shaking periodically during activation period. These methods apply for batch system but for continuous system, activation should be done by flushing the catalyst with fresh alcohol for a period of time prior to contacts with a subsequent amount of feedstock with or without agitation and heat.

Furthermore, the catalyst can be reused up to 15 to 20 times before its reactivity declines. Catalyst with reduce reactivity can be fully regenerated by calcination (Lin et al., 2011).

2.7 Conclusion

Depletion of fossil fuel has led to finding an alternative which is the production of biodiesel from rubber seed oil. Biodiesel production involves extraction of oil from rubber seeds, characterisation of the crude oil, reduction of FFA and reaction. Besides that, the use of basic solid catalyst will eliminate problems associated with neutralisation, separation and removal of catalyst. The methods will be discussed in detail in Chapter 3.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

This chapter will discuss the methods used for rubber seed oil extraction and characterisation, cement clinker activation and characterisation, transesterification and separation and finally the characterisation of fatty acid methyl esters (FAME).

3.2 Processes

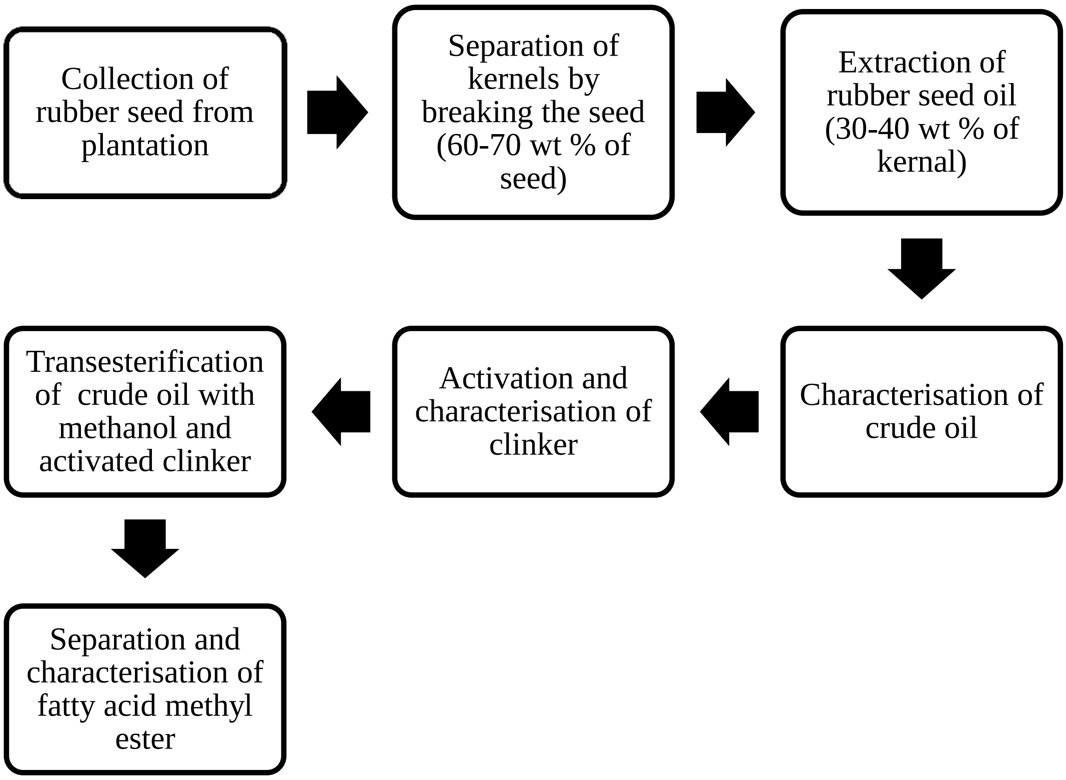


Figure 3.1: Block diagram showing the whole process of biodiesel production from rubber seed oil

3.3 Oil extraction

Fresh rubber (Hevea brasiliensis) seeds were collected from the Rubber Plantation around Gambang, Kuantan and Ipoh, Perak. The seeds were washed to remove dirt and mud and then were dried in the oven at 45 °C for 24 hours. The kernels were then removed by cracking the seeds manually. The shelled seeds were then dried again overnight in oven at 45°C. The dried were then crushed using a laboratory blender until it becomes powder. RSO was extracted using two methods; Soxhlet extraction and microwave assisted extraction. The efficiency of extraction based on two parameters; time and efficiency was evaluated. In Soxhlet extraction procedure, 50 g of crushed seed was packed in a thimble and the oil was extracted with n-hexane for 2hours. In

Soxhlet extraction methods, the oil was isolated from n-hexane using rotary evaporator. In microwave assisted method, n-hexane was used as extraction solvent. Temperature was set at slightly below the boiling point of n- hexane at about 64 °C, power at 200 W at 20 minutes intervals for 1 hour.

Rubber plantation in Kuantan

Rubber Seed Overview

Crushed seeds prepared for extraction

Soxhlet extraction

Figure 3.2: Pictures related to rubber seed collection and extraction of crude oil

3.4 Characterisation of Rubber Seed Oil

Crude RSO was subjected to a few characterisation based on ASTM D 6751 specifications. Specific gravity, acid value, free fatty acid composition, calorimetry and refractive index tests were done on crude oil. The following tests were done based on ASTM Standards:

3.4.1 Specific Gravity

Specific gravity was measured using a calibrated Pycnometer 1340. The value obtained will be compared with the value of FAME. Approximately 5 g of oil was used.

3.4.2 Acid Value

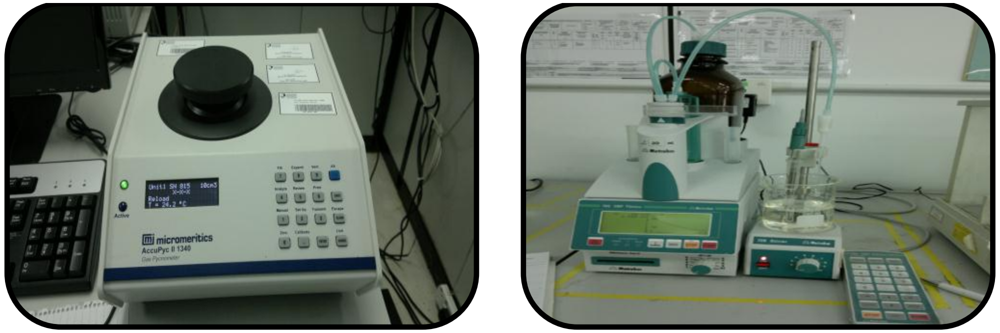
Acid value of crude RSO was determined using Potentiometer model 785 with stirrer model 728 following D 664 standard. Acid value is the sum of all acidic components in the crude oil to indicate the level of free fatty acid (FFA). Acid number will also indicate the amount of catalyst needed to neutralise the acid content of oil so that the value is below 0.50 mg KOH/ g. KOH solution of 0.1 mol/L was prepared as titrating solution.

3.4.3 Calorific value

The heating value was obtained using Bomb Calorimeter model AC equipped with water bath and oxygen controller.

3.4.4 Free fatty acid composition

Fatty acid composition of RSO was determined by using Gas Chromatography model 5975 C according to ASTM D-1983 test method.



Gas Pycnometer

Potentiometer

Bomb Calorimeter

GC-MS

Figure 3.3: Equipment used in testing procedures

3.5 Clinker Activation and Characterisation

The process flow below in Figure 3.3 shows clinker preparation. Clinker was obtained from Pahang Cement Sdn. Bhd. Clinker was collected from the conveyer belt and was then crushed using the jaw crusher to obtain clinker size of below 5mm. 100 g of crushed clinker was then grinded using mortar and pestle and all the 100 g of clinker was passed through 200 µm sieve. X-ray analysis as well as Blaine test for surface area was done for the prepared clinker.

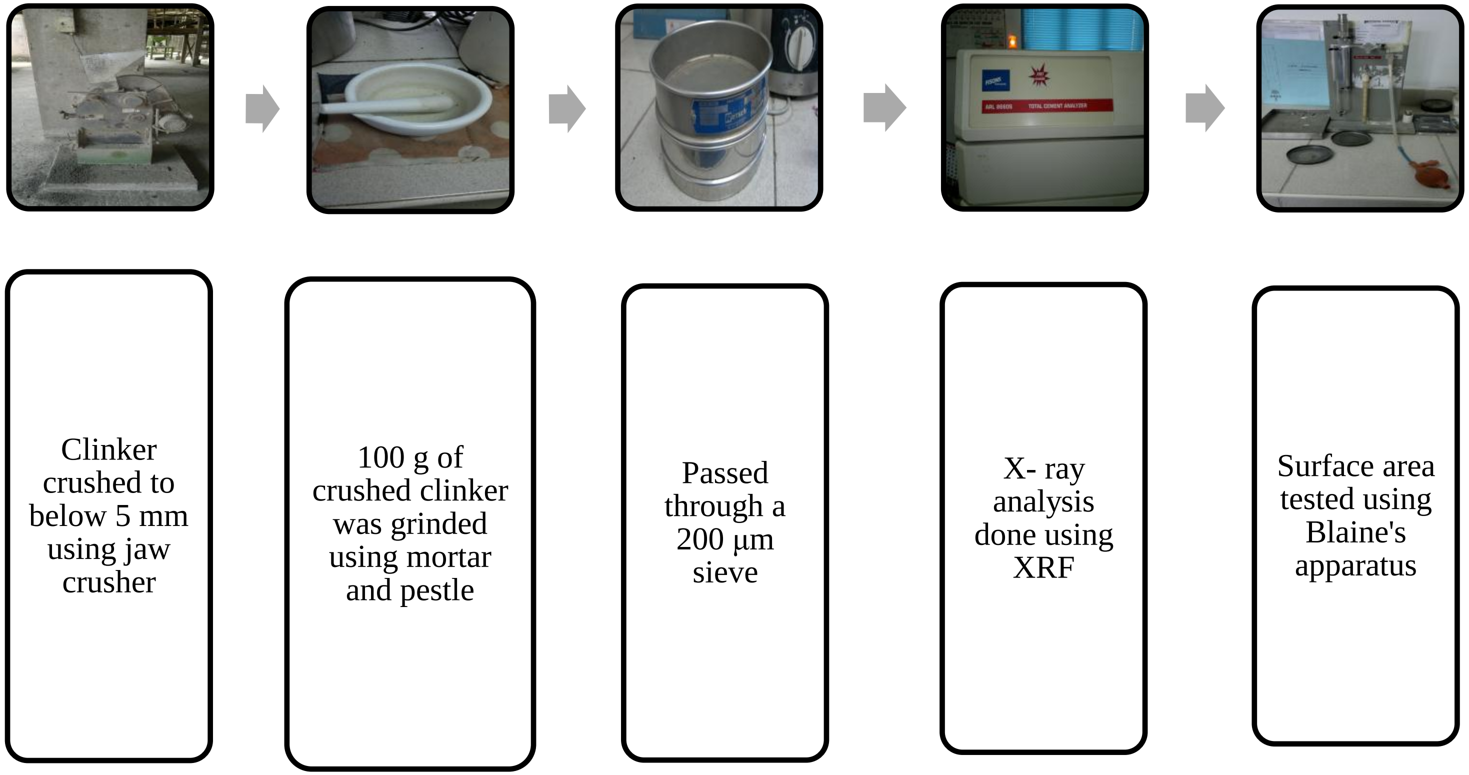


Figure 3.4: Process flow for clinker preparation and characterisation

Clinker activation was done at various temperature, activation time, catalyst loading and methanol to catalyst ratio. Activation of catalyst was done by dispersing the clinker into the methanol at various parameters as shown below in Table 3.1.

T**able 3.1**: Activation parameters for clinker

Activation temperature	Activation time	Catalyst loading (methanol: catalyst ratio)	Catalyst to methanol ratio
Room temperature (25 °C)	30 minutes	1:100 (1.188 g)	1:100 (38 ml)
35 °C	1 hour	1:200 (0.594 g)	1:200 (75 ml)
45 °C	4 hours	1:300 (0.396 g)	1:300 (113 ml)
55 °C	12 hours	1:400 (0.297 g)	1:400 (150 ml)
64.7 °C	24 hours	1:500 (0.238 g)	1:500 (188 ml)

NOTE:

1. At various activation temperatures, the following are kept constant: activation time (4 hours), catalyst loading (0.3 g) and catalyst methanol ratio (1:400; 150 ml).

2. At various activation times, the following are kept constant: activation temperature (64.7 °C), catalyst loading (0.3 g) and catalyst methanol ratio (1:400; 150 ml).

3. At various catalyst loadings, the following are kept constant: activation temperature (64.7 °C), activation time (4 hours) and catalyst methanol ratio (1:400; 150 ml).

4. At various catalyst methanol ratios, activation temperature (64.7 °C), activation time (4 hours) and catalyst loading (0.3 g).

Activation was done with constant agitation to produce a better effect. SEM analysis was done to study the activation and conclude the optimum activation parameter morphologically for transesterification.

3.6 Transesterification

Transesterification process of rubber seed oil using activated clinker includes the transesterification setup, activation of clinker, reaction and separation of fatty acid methyl ester (FAME) from glycerol layer and used catalyst.

Prior to transesterification process, clinker is first activated with methanol. Four different catalyst loading were tested using different clinker-to-oil ratios (0.5 %, 1.5 %, 2.5 % , 3.5 %, 4.5 % and 5.5 % w/v) were used to investigate their influence on the methyl ester yields of the oils. All the reactions were carried out in the round bottom flask, which were immersed in an aluminum water bath placed on the plate of magnetic stirrer of 400 rpm. The temperature and the reaction time for all process were maintained at 60.0 ± 0.5 °C and for 1 h, respectively. Methanol to oil ratio is made constant at 6:1 ratio. After the reaction, the mixture was allowed to settle overnight before separating the top layer containing unreacted methanol, impurities and maybe unreacted RSO. Glycerol and catalyst appeared in the bottom layer and the middle layer contained FAME. No further purification step such as washing was needed as the catalyst traps the glycerol and other impurities. This is a waterless procedure.

3.7 Characterisation of FAME

The separated methyl ester layer was subjected to testing according to ASTM 6751 standard. GC analysis, density, acid value was tested.

3.7.1 GC Analysis

The FAME was analysed using GC-MS equipped with a flame ionization detector (FID) and a BFSP-0677-02 packed column (2 m x 0.32 mm x 0.25 µm). Methyl heptadecanoate was used as the internal standard to determine the amounts of products. The GC oven was kept at 150 °C for 5 min, heated at 5 °C/min up to 240 °C, where it was kept for 6 min, and a total analytical time was 29 min. The carrier gas was helium (0.7 ml/min).The analysis of biodiesel for each sample was carried out by preparing 2 % dilution (dissolving 20 µl of biodiesel sample into 980 µl of HPLC grade Hexane and injecting 2 µl of this solution in GC. The yield of biodiesel (FAME) with respect to rubber seed oil was calculated from the content of methyl esters analysed by GC with the following equation:

$$Yield\ (\%) = \frac{(\sum Concentration\ of\ each\ FAME\ component) \times (Volume\ of\ product\ layer) \times 100\%}{Total\ weight\ of\ oil\ in\ the\ sample}$$

3.8 Conclusion

It is hoped that all the test procedures done complies with ASTM D6751 biodiesel standard. Results will be discussed in Chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter will discuss the results obtained from (a) extraction of rubber seed oil, (b) rubber seed oil characterization, (c) catalyst activation and characterization, (d) transesterification of rubber seed oil with activated cement clinker.

4.2 Seed Characteristics Of Rubber Seeds

4.2.1 Physical Properties

Table 4.1: The physical properties of Jatropha, Karanja, Castor and Rubber seeds

Characteristics	**Rubber**	**Rubber**	**Jatropha**	**Karanja**	**Castor**
	This work	Haque et al. (2009)			
Seed shape	Ellipsoidal	Rectangular	Cylindrical	Circular	Cylindrical
Average length (mm)	28	21.5	17.1	17.9	11.8
Average weight (g)	3	4.3	0.8	1.2	0.2
Average width (mm)	17	18.8	9.6	14.4	6.3
Moisture content (wt %)	19	14.2	9.1	10.9	10.1
Oil content (dry basis wt %)	33*	38.9	32.4	31.8	67.7

* Based on Microwave Extraction

In comparison to other seeds, rubber seeds are larger in size due to the presence of hollow space between the endosperm and the outer hard shell. According to Haque et al. (2009), even Jatropha seeds have large bulk densities just like rubber seeds due to the same reason of having hollow space. The endosperm of both Karanja and Rubber is found to be spongy. It is evident form the crushing process that rubber seeds have high hardness strenght though it was not tested. But according to Haque et al. again, rubber seeds have the highest hardness value of 8.6 kg compared to all the other other seeds. This is supported by the reason that rubber seeds are covered by a thick and hard shell. In this work done, it can be concluded that the hard shells consist of almost half the weight of the seeds. When a sample of 500 g of seeds are crushed, only 251.1 g of seeds without the shells are obtained which gives roughly of only 50.22 % of the initial weight. It can be concluded that rubber seeds require much higher load to crack.

Rubber seeds During crushing Crushed seeds

Hard outer shells Oil + Hexane in Soxhlet

Figure 4.1: Rubber seeds before, during and after crushing

4.2.2 Moisture Content And Oil Content Analysis

Table 4.2: Moisture and oil content analysis of rubber seeds

Weight of empty beaker (g)	270.64
Weight of beaker + crushed seeds (g) Before drying	770.64
Weight of beaker + dried seeds overnight at 60 °C (g)	675.14
Weight of sample for extraction (g)	400
Weight of oil after extraction (g)	133.5

Compared to the work done by Haque et al., moisture content of rubber seeds in this work is higher (19 % compared to 14.2 %). In general, moisture content of rubber seeds is higher than that of Jatropha, Karanja and Castor seeds. For the oil content, it is justified on why is rubber seeds' oil content is much lower than of castor seeds. It is due to the reason that rubber seeds is made of hard shell and hollow spaces unlike castor seeds which are made of soft endosprem with soft shell.

4.3 Extraction Efficiency

The folowing table is to compare the extraction efficiency of rubber seed oil using Soxhlet and Microwave. There is vast differences in yield obtained and extraction time.

Table 4.3: Comparison between Soxhlet and Microwave extraction

Parameters	Soxhlet Extraction	Microwave Extraction
Crushed seeds inlet (g)	100	250
Hexane needed (ml)	250	500
Extraction time (min)	240	30
Yield (g)	28	82.5
Yield (%)	28	33

Extraction of rubber seed oil using microwave extraction is found to be more efficient as it is time saving and the yield is also higher. In both extraction methods, the extracted oil is collected in the hexane. Oil is soluble in hexane. Therefore, the oil and hexane is separated using Rotary Evaporator. Separation is based on difference in boiling point. Hexane has a boiling point of 69 °C. At temperature of 55 °C, hexane will start vaporising and will be collected separately. In both methods, hexane can be recycled as its function as extraction solvent does not deteriorate with multiple extractions. The advantages of using microwave extractor outweigh the use of Soxhlet extraction as handling of microwave is even easier. Temperature and pressure control is made easier. There is no difficult assembling and worries of hexane vaporising into the air. But care need to be taken when adjusting the power as not to increase above 200 W. localising heating happens in the microwave. If power is too high, pressure can build up in the glass container and the content inside can explode.

4.4 Clinker activation and characterisation

4.4.1 Clinker characterisation

The chemical composition of clinker was analysed using XRF. The results of X-ray analysis are as follows:

Table 4.4: Clinker analysis (oxide weight %)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	P_2O_5	TiO_2	Total
66.61	21.92	6.33	4.00	0.73	0.46	0.92	0.12	0.03	0.30	101.42

Based on the analysis, it can be observed that clinker has a high amount of CaO which is about 66.61%. This value can also be found in literature review; research by WHM Microanalysis Consultants (2005). This high percentage of CaO attributes to its property as a good solid base catalyst. Besides that, surface area test was done using Blaine’s apparatus.

Surface area of grinded clinker is calculated according to the following formula:

$t = 149.5\ s$

$$\frac{S}{A} = \sqrt{t} \times 456.96 \qquad \text{Eq (4.1)}$$

S/A = 5587.26 cm^2/g @ 0.56 m^2/g

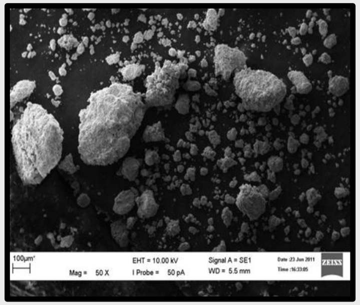
in which 456.96 is the calibrated value of Blaine's apparatus.

Results show that the grinded clinker which is passed through 200 µm sieve has a surface area of 0.56 m^2/g compared to 0.2 m^2/g (Lin et al., 2011) using cement kiln dust. Using clinker as a heterogeneous catalyst gives many advantages. Reaction rate is faster and yield is also higher because of high surface area of clinker. The clinker can be recovered after reaction and can be recycled a various times before the effect wears out but it can be calcined again before re- use. CaO derived base as in clinker is very promising as it exhibit low solubility in methanol and is also less toxic compared to other alkaline earth oxides.

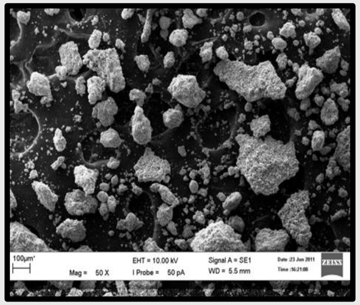
4.4.2 Catalyst activation

Activated catalyst was observed using surface scanning electron microscope. The pore distribution of active clinker can be observed from the SEM results. Figures 4.2 to 4.4 shows the SEM pictures taken for different clinker activation parameters.

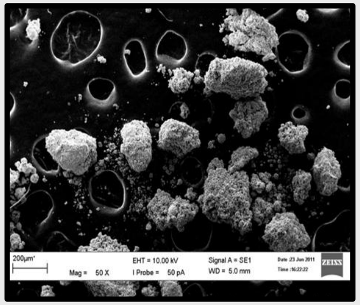
Figure 4.2: SEM photos for clinker at different activation temperature (clinker distribution)



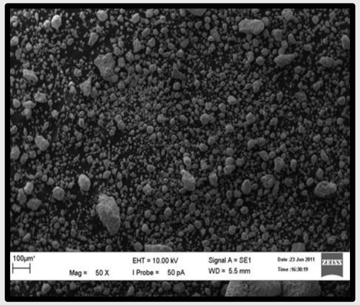
35 °C 50x



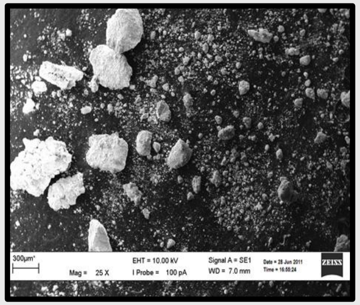
45 °C 50x



55 °C 50x

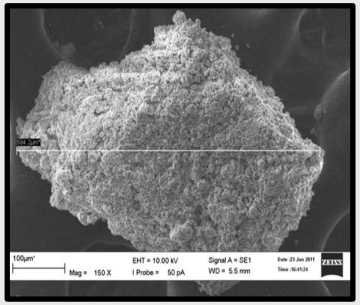


64.7 °C 50x

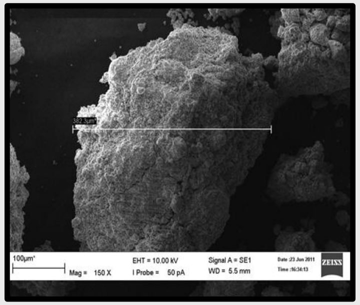


Original clinker

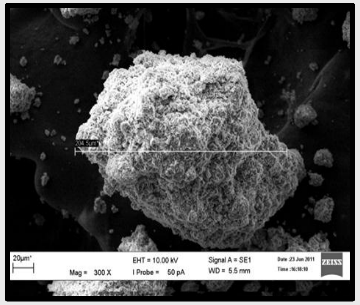
Figure 4.3: SEM photos for clinker at different activation temperature (particle size)



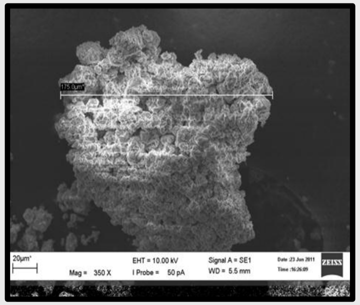
25 °C 150x



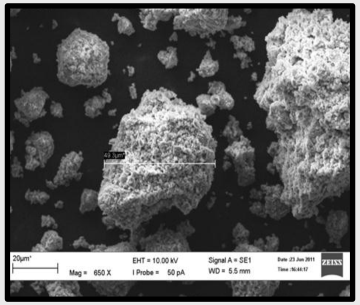
35 °C 150x



45 °C 150x

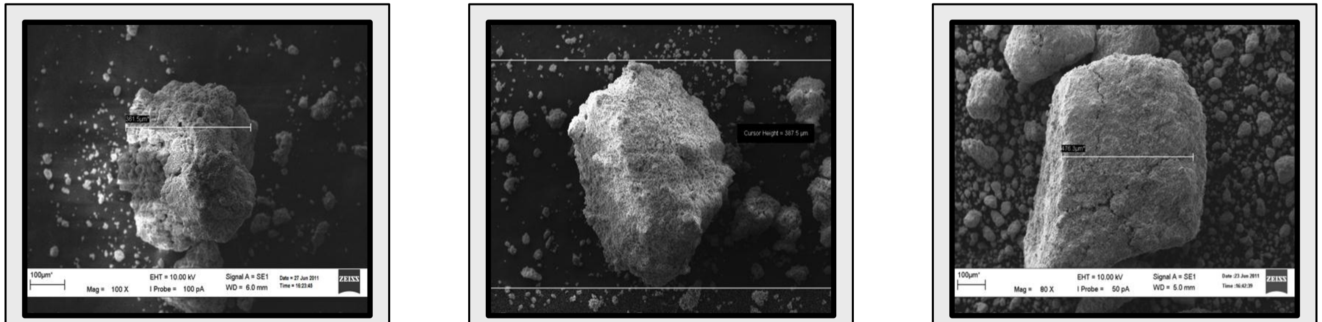


55 °C 230x



64.7 °C 650x

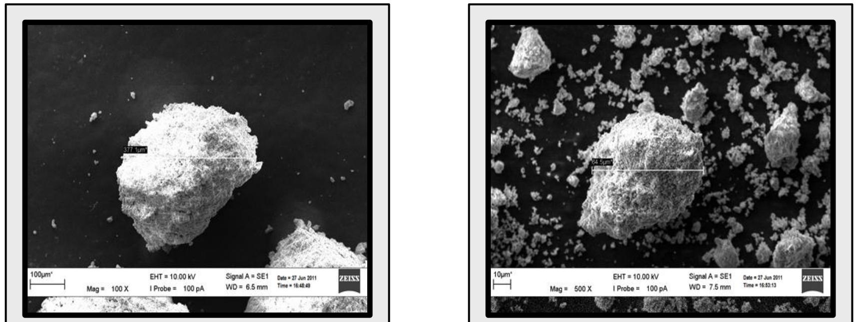
Figure 4.4: SEM photos for clinker at different activation time (particle size)



30 minutes 100x

45 °C 50x

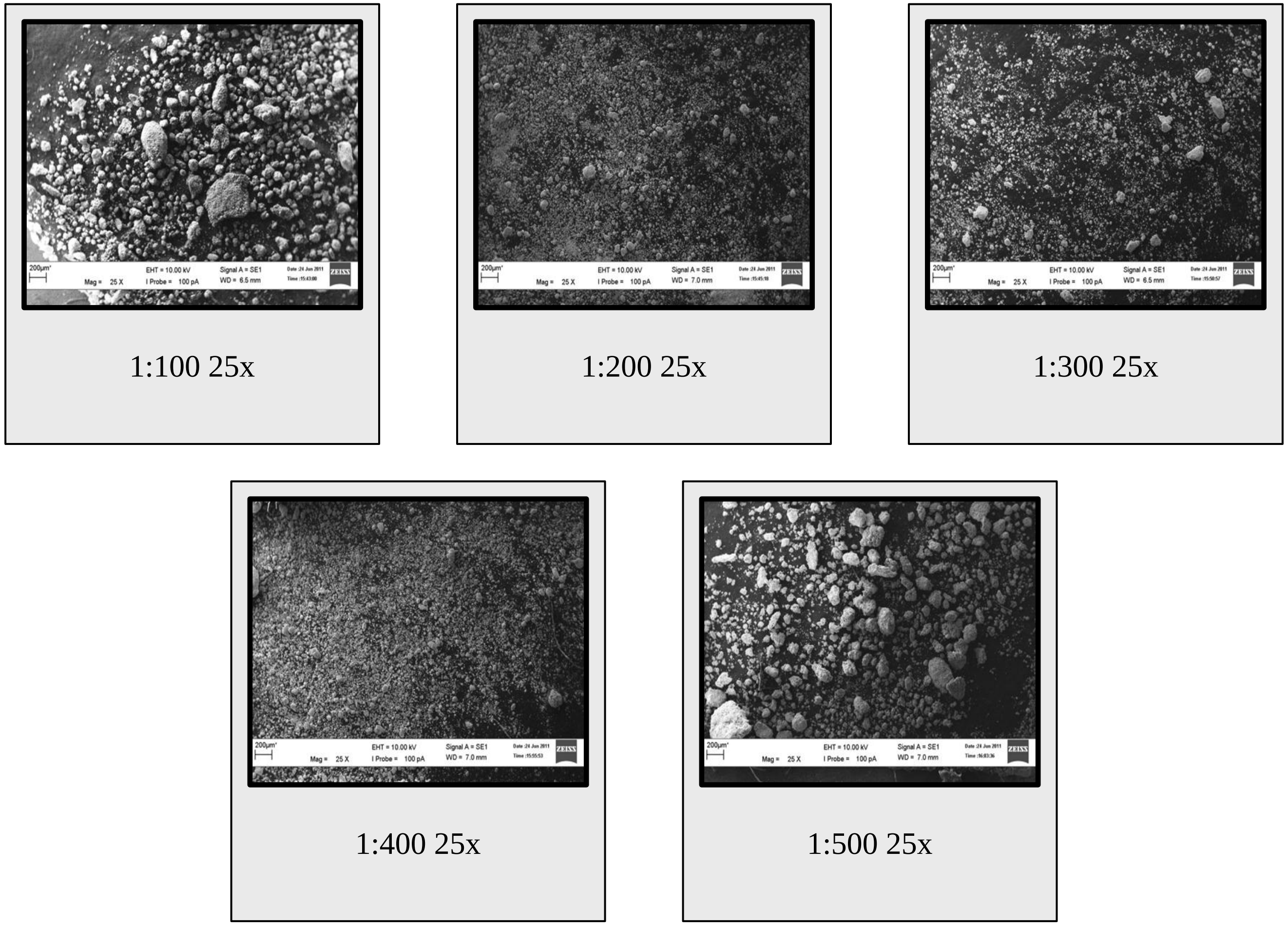
4 hours 80x



12 hours 100x

24 hours 500x

Figure 4.5: SEM photos for clinker at different clinker loading, methanol: clinker (particle distribution)



1:100 25x

1:200 25x

1:300 25x

1:400 25x

1:500 25x

From Figure 4.2, it can be observed that at 64.7 °C, the activated clinker is distributed well with particulars having almost similar size. At temperature 35 °C, 45 °C and 55 °C, the particles are not well distributed and still form large sized particulars with varying diameter. A vast difference can be observed for an inactivated clinker and activated clinker at 64.7 °C. These differences may be due to the fact that methanol's reactivity is the best at its boiling point. Figure 4.3 gives a clearer overview of the activated clinker in terms of particle size. The average size is taken; 584.2 μm, 382.3 μm, 204.5 μm , 175.0 μm and 49.3 μm for the particles at temperatures 25 °C, 35 °C, 45 °C, 55 °C and 64.7 °C respectively. Activation at 25 °C can be considered as the clinker being not activated at all due to no heating. From the particle size, it can be concluded that clinker activated at 64.7 °C has the particle appearance in terms of size and distribution which will contribute to better reactivity due to higher surface area for reaction.

From Figure 4.4, it can be observed that particles have an average size. 24 hours activation gives the smallest particles but 1 hour activation is preferred due to shorter activation period. Comparing activation time of 30 minutes, 1 hour, 4 hours and 12 hours with particle size of 361.5 μm, 387.5 μm, 476.3 μm and 377.1 μm respectively, at 1 hour activation period is chosen to be optimum.

From Figure 4.5, the clinker distribution at different catalyst loading can be observed. It can be observed that at 1:400 ratio of methanol to clinker, the activated clinker is distributed well with particulars having almost similar size. At 1:100, 1:200, 1:300 and 1:500, the particles are not well distributed and still form large sized particulars with varying diameters. At 1:500 ratios, the particles seem to be larger probably due to very high volume of methanol compared to mass of clinker dispersed. According to Lin et al. (2011), the use of higher amounts of methanol results in a faster reaction.

It can be concluded from the SEM analysis that the optimum conditions for clinker activation is at 64.7 °C for 1 hour with 1:400 clinker-methanol weight ratio.

4.5 Crude Rubber Seed Oil Characterisation

Determining fatty acid composition is an important thing in this research. The properties of the triglyceride and the biodiesel fuel are determined by identifying and quantifying the amounts of each fatty acid that are present in the molecules. The physical characteristics of fatty acids and triglycerides are determined by the double bonds and chain length (Mittelbach and Remschmidt, 2004). This composition plays a vital role in cetane number and cold flow properties of biodiesel and is not altered by transesterification (Ramos et al., 2008). There are three main types of fatty acids that can be present in a triglyceride which is saturated (Cn: 0), monounsaturated (Cn: 1) and polyunsaturated with two or three double bonds (Cn: 2, 3). According to Gunstone (2004), vegetable oil should have low saturation and low polyunsaturation i.e. be high in monounsaturated fatty acid. Saturation fatty acid methyl esters increase the cloud point, cetane number and improve stability whereas more polyunsaturates reduce the cloud point and cetane number and stability (Ramadhas et al., 2004).

Gunstone further stated that vegetable oils that are rich in polyunsaturated such as linoleic and linolenic acids, such as soybean, sunflower, tend to give methyl ester fuels with poor oxidation stability. On the other hand, vegetable with high degree unsaturation tend to have high freezing point. This oil will have poor flow characteristic and may become solid (e.g. palm oil) at low temperatures though they may perform satisfactorily in hot climates. The fatty acid composition and the important properties of rubber seed oil in comparison with soy bean oil are given Table 4.4.

Table 4.5: Properties of rubber seed oil from this work in comparison with other work

Property	Rubber seed oil		Soy bean oil
	This work	**Ramadhas et al. (2004)**	
Fatty acid composition (%)			
(i) Palmitic acid $C_{16:0}$	10.29	10.2	3.49
(ii) Stearic acid $C_{18:0}$	8.68	8.7	0.85
(iii) Oleic acid $C_{18:1}$	20.07	24.6	64.4
(iv) Linoleic acid $C_{18:2}$	58.50	39.6	22.3
(v) Linolenic acid $C_{18:3}$	-	16.3	8.23
Specific gravity	0.9201	0.91	0.914
Calorific value (MJ/kg)	38.96	37.5	37.6
Acid value (mg KOH/g)	35.14	34	1.14

The rubber seed oil in this work consists of 18.97 % saturation comprising of palmitic and stearic acids and 78.57 % unsaturation comprising mainly of oleic and linoleic acids. Linolenic acid is not present in the analysis. Both the soy bean oil and rubber seed oil are oleic: linoleic dominant. Therefore, there is higher degree of unsaturation in these oils. Oleic acid is monounsaturated fatty acid whereas linoleic acid is polyunsaturated fatty acid. The fatty acids in rubber seed oil from this work are very much comparable with Ramadhas et al.'s besides the value for linoleic acid and the absence of linolenic acid.

The absence of linolenic acid is probably due to improper method implied for GC-MS. Normally linolenic acid can be detected from the 15th to the 20th minute of the retention time probably if a different method was used. Example; temperature programming of 100 °C for 2 min, 33 °C for 33 min and 220 °C up to the end is used with temperature rate changes of 40 °C/min, injector temperature 200 °C and detector temperature °C and helium gas as carrier. Besides that, another possible reason is justified by Ramadhas et al. (2004) that type and percentage of fatty acids contained in vegetable oil depends on the plant species and on the growth conditions of the plant.

According to Abramovic and Kloufutar (1998) and Fasina et al. (2006), oil oxidation is influenced by the fatty acid composition of the respective oil. Oils that are more unsaturated are oxidized more quickly than less unsaturated oils. They also reported that viscosity increases with increase in amounts of monounsaturated fatty acid and vice versa with polyunsaturated acid.

If rubber seed oil is compared with soy bean oil, acid value is much higher. Therefore, crude oil should be refined before transesterification process in order to prevent soap formation.

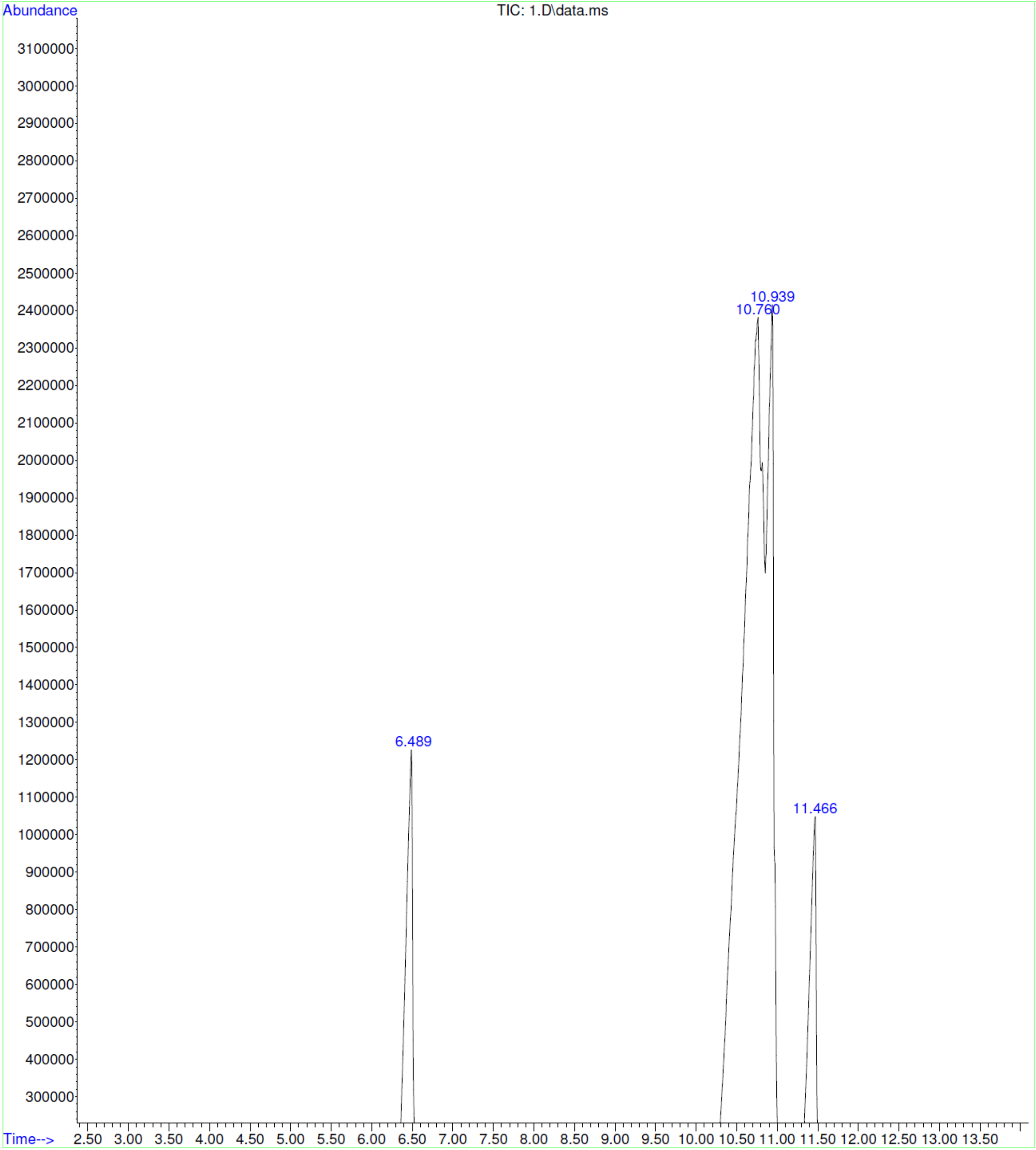


Figure 4.6: Spectra of FFA content in RSO

4.6 Factors affecting the transesterification

There are various factors that affect transesterification for example, methanol to oil ratio, reaction temperature and catalyst loading.

4.6.1 Influence of molar ratio

The stoichiometry of transesterification reactions requires 3 mole of alcohol for every mole of triglyceride in order to produce 3 mole of methyl ester and 1 mole of glycerol as by product. The amount required in actual is much more in order to complete the reaction and attain a higher yield. Higher molar yield is required to complete reaction at a faster rate. In this work, the molar ratio of methanol to oil is made constant at 6:1. For every mole of oil, 6 mole of methanol will be reacted. In this work, the catalyst will first be dispersed in the methanol before putting in the oil for further reaction. According to Ramadhas et al., lower molar ratios requires longer reaction period. With further increase in molar ratio above 9:1 ratio, the conversion efficiency more or less remains the same. There is no qualm about using extra methanol as the excess methanol will move over the ester layer. Excess methanol is separated by water washing and using rotary evaporator based on difference in boiling point theory. Excess methanol should be removed or else it affects biodiesel by decreasing the flash point.

4.6.2 Effect of Catalyst Loading

Table 4.6: Yield of FAME from rubber seed oil at various concentration levels

Catalyst amount (g)	Catalyst concentration (% w/v)	Product volume (ml)	*FAME yield fraction	FAME concentration (%)
0.2	0.5	18.6	0.465	22.97
0.6	1.5	20.4	0.510	64.57
1.0	2.5	23.1	0.578	87.25
1.4	3.5	30.0	0.75	96.65
1.8	4.5	25.3	0.633	93.15
2.2	5.5	21.3	0.533	66.00

The catalyst concentration level β was calculated based on the formula:

B = (weight KOH)/(volume oil)*100 Eq (4.1)

Biodiesel yield fraction γ was obtained from:

γ = (Product Volume)/(Oil volume) Eq (4.2)

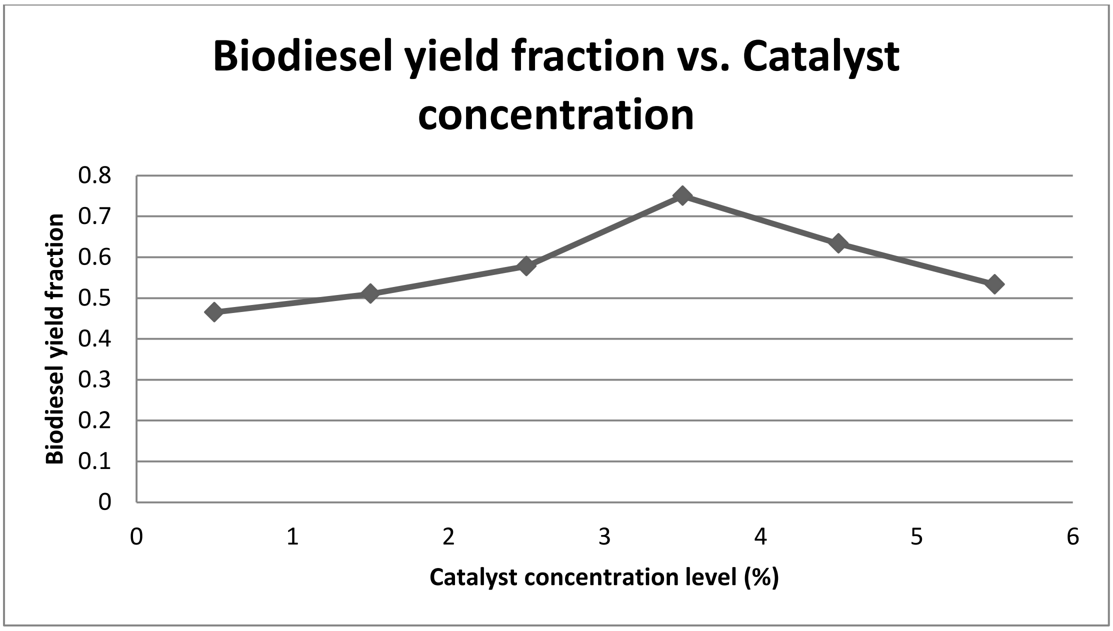


Figure 4.7: Biodiesel yield versus catalyst concentration

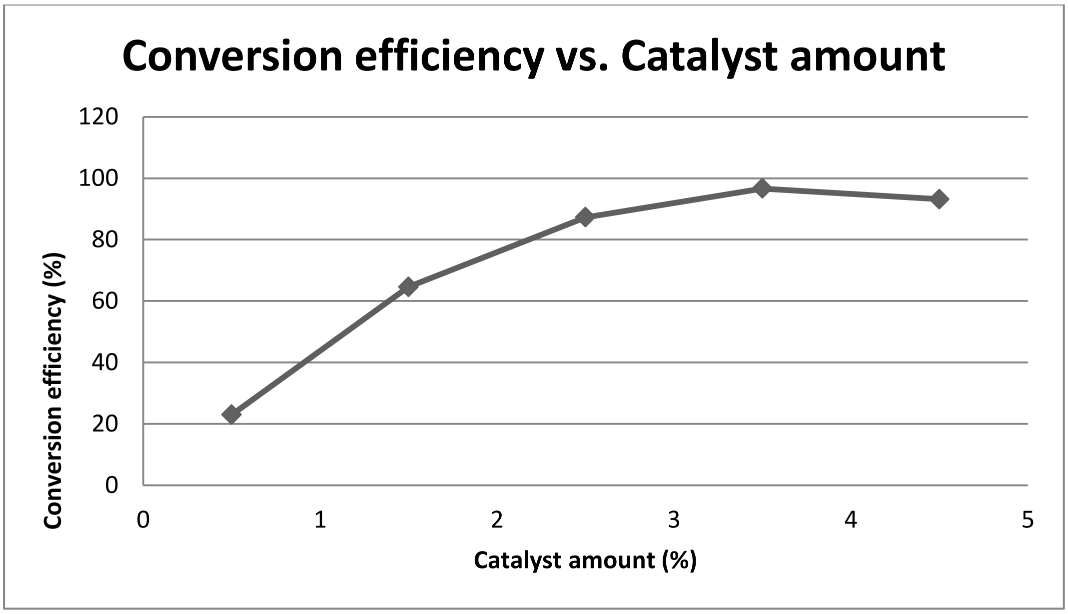


Figure 4.8: Effect of activated clinker amount on conversion efficiency

From table 4.6, it is observed that the product volume increased steadily from 0.5 % w/v concentration of the activated clinker until it peaked at 3.5 % w/v of catalyst concentration and thereafter, a decrease was observed. It is therefore clear increment in concentration level of the catalyst would not yield further volume increase in biodiesel obtainable from rubber seed oil. This could be explained from the viewpoint of Darnako (1999) on the reversible nature of the transesterification process. Catalyst concentration levels greater than 3.5 % may have favoured the backward reaction; the formation of glycerol.

4.6.3 Effect of reaction temperature

The reaction temperature for transesterification in this work is kept constant at 60 ± 0.5 °C which is the boiling point of methanol. Reaction was done under reflux to avoid the vaporizing methanol to escape into the environment. Ramadhas et al. has stated that reaction temperatures greater than 60 °C should be avoided for rubber seed oil as it accelerates saponification of the glycerides before the completion of alcoholysis. Generally, as the reaction temperature increases, the rate of reaction increases as catalyst is affected by temperature through the Arrhenius equation.

4.6.4 Effect of reaction duration and agitation

The speed of stirrer was set at 400 rpm. Stirring at constant rate is important in order to achieve perfect contact between the reagents and oil during transesterification (Ramadhas et al., 2004). Duration time is set to 1 hr to support the catalyst loading effect while keeping other parameters constant.

4.7 Fatty Acid Methyl Ester Characterisation

Transesterification of RSO with activated clinker produces fatty acid methyl ester and glycerol. The complete transesterification forms three distinguished layers as below:

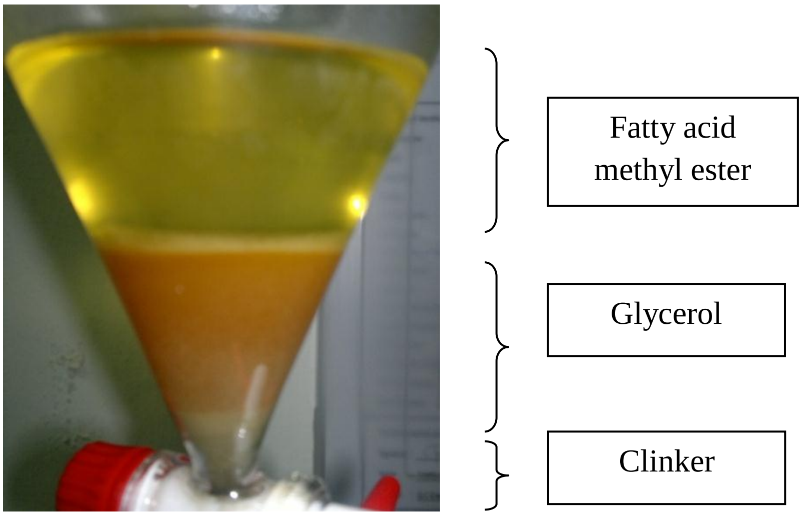


Figure 4.9: Three distinguished layers after transesterification

The fuel properties of FAME produced in this work is compared with other work done in Table 4.7.

Table 4.7: Properties of methyl esters of rubber seed oil

Property	Rubber seed oil methyl ester		Soy bean oil methyl ester
	This work	Ramadhas et al. (2004)	
Specific gravity	0.8548	0.874	0.885
Calorific value (MJ/kg)	38.87	36.50	39.76
Acid value (mg KOH/g)	1.7952	0.118	N/A

NA, Not available

Only three fuel properties were tested in this work and the properties are quite comparable to those of other work and diesel itself. All the properties are within the biodiesel standard of ASTM 6751-02. If the values in the above table are compared with the crude oil before transesterification, the specific gravity decreased from 0.9201 g/cm^3 to 0.8548 g/cm^3. Acid value also decreased tremendously from 35.14 mg KOH/g to 1.7952 mg KOH/g but the value is slightly off the biodiesel which should be below 0.8. This is because no refining step was done to bring down the acid value. If bleaching was done, then probably the acid value would have been below 0.8 mg KOH/g. The chromatographic analysis supports that the biodiesel contains large amount of C_{18}. RSO FAME in work contains 14.47 % methyl palmitate, 38.38 % ethyl linoleate, 18.17 % of methyl stearate and 25.63 % of ethyl oleate. The present results obtained show that, the transesterification process improved the fuel properties of the oil with respect to specific gravity and acid value. The comparison of these properties with diesel shows that the methyl ester has a relatively closer fuel property values to that of diesel (than that of oil). The calorific values of methyl esters are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine.

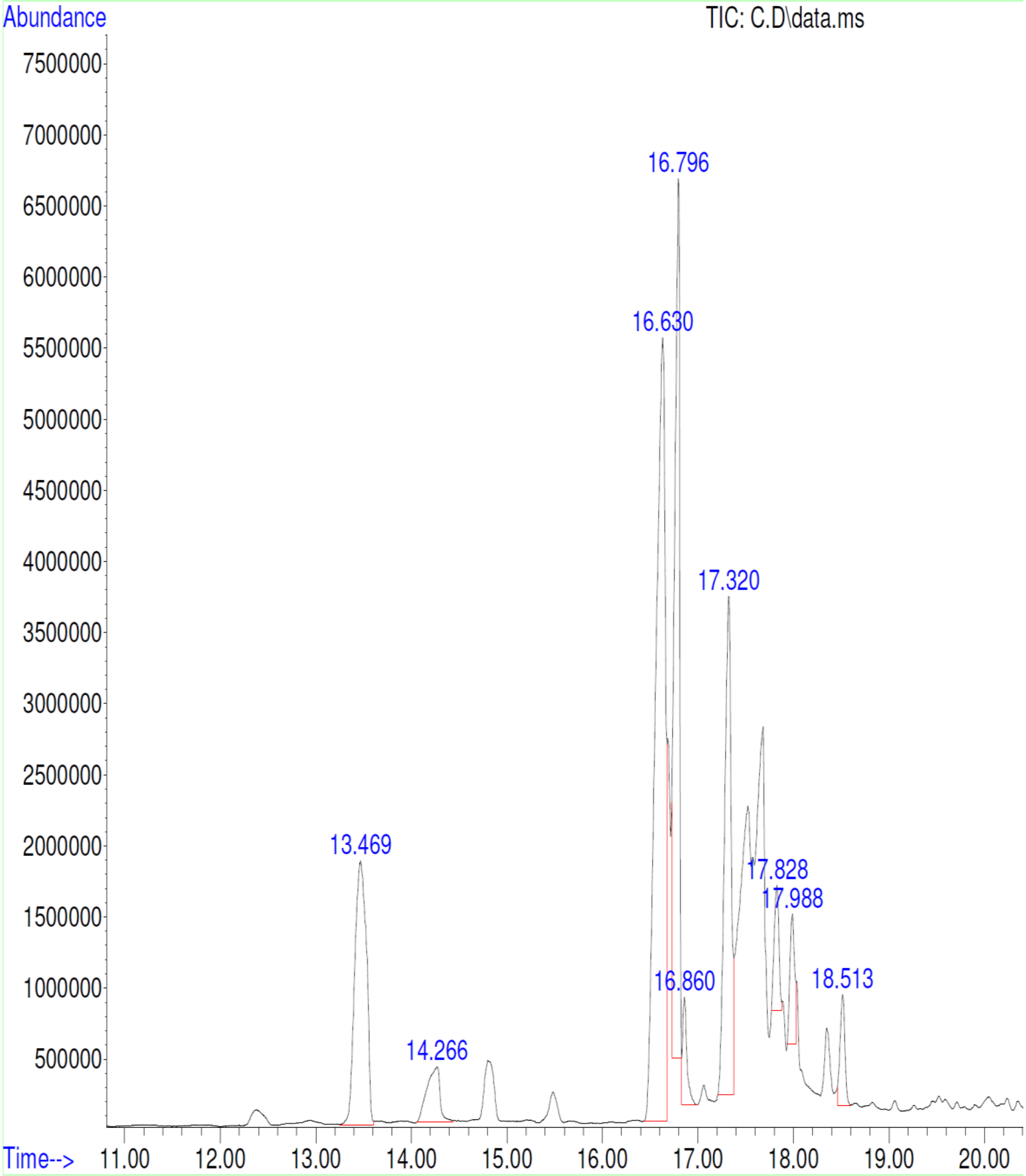


Figure 4.10: Spectrum of RSO FAME

4.8 Conclusion

In conclusion, the tested properties of methyl esters of rubber seed oil are found to be in reasonable agreement with ASTM 6751.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Production of biodiesel from widely available feedstock which is of vegetable origin and a non-edible is investigated in this study. Previous researches show that feedstocks with high FFAs could not be transesterified with the commercially available alkaline catalyst transesterification process. Utmost justification for this is the formation of soap which prevents the separation of glycerin and ester. Potential of cement clinker is discovered as a suitable heterogeneous solid base catalyst to transesterify FFA oils into esters. High CaO content makes clinker a highly usable catalyst. Its activated procedure is very easy and it can be re-used numerous times. Transesterification process converts the FFA its mono-esters and glycerol. The effect catalyst loading is studied while making the methanol to oil ratio, reaction temperature, stirring speed and reaction duration constant. The morphology of the catalyst itself is studied by comparing SEM pictures of before and after applying various activation parameters. It has been found that the conversion efficiency is strongly affected by the catalyst loading. Methanol to oil molar ratio of 6:1, reaction temperature at 60 ± 0.5 °C, catalyst loading of 3.5 w/v % at constant stirring at 400 rpm for 1 hour favors the completion of alkaline catalyzed esterification process. The maximum ester conversion achieved is 96.65 % at these optimum conditions. The present analysis reveals that biodiesel from unrefined rubber seed oil is quite suitable as an alternative to diesel. However, further research and development on additional fuel property measures, long-term run and wear analysis results support the choice of using rubber seed oil as a potential alternative of diesel fuel. The use of cement clinker is also a solution for expensive metal catalyst. This research is an opportunity to optimise waste for the country’s revenue.

5.2 Recommendations for Future Research

Firstly, refining or bleaching crude rubber seed oil will definitely bring down the acid value to below 0.8 mg KOH/g as stated in the ASTM D6571 biodiesel standard. High acid value can cause corrosion in engine. Secondly, a proper method for GC-MS analysis should be chosen so that all the FFA and FAME composition is detected accurately in the oil sample. Thirdly, more fuel properties tests like viscosity, cloud point, pour point etc. should be done in the future and possibly an engine test to assure the suitability of biodiesel derived through this method to be used as a fossil fuel substituent. Fourthly, research can be done to check the use of other cement intermediate products as catalyst as it all contains CaO but in different percentages. Examples of materials that can be tried is limestone powder and EP dust.

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micromeritics®

Sample: CRSO
Operator:
Submitter:
Bar Code:
File: C:\1340\DATA\CRSO.SMP

Analysis Gas: Helium
Reported: 11/20/2011 12:20:56AM
Sample Mass: 5.0161 g
Temperature: 24.77 °C
Number of Purges: 5

Analysis Start: 11/19/2011 5:24:15PM
Analysis End: 11/19/2011 6:38:31PM
Equilib. Rate: 0.005 psig/min
Expansion Volume: 5.0000 cm^3
Cell Volume: 10.0000 cm^3

Summary Report

Sample Volume
Average: 6.7780 cm^3
Standard Deviation: 0.0084 cm^3

Sample Density
Average: 0.8201 g/cm^3
Standard Deviation: 0.0009 g/cm^3

Sample: RSO-B100
Operator:
Submitter:
Bar Code:
File: C:\1340\DATA\RSO-B100.SMP

Analysis Gas: Helium
Reported: 11/19/2011 10:59:34PM
Sample Mass: 5.2065 g
Temperature: 25.08 ℃
Number of Purges: 5

Analysis Start: 11/19/2011 10:19:28PM
Analysis End: 11/19/2011 10:58:20PM
Equilib. Rate: 0.005 psig/min
Expansion Volume: 5.0000 cm³
Cell Volume: 10.0000 cm³

Summary Report

Sample Volume
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Standard Deviation: 0.0022 cm³

Sample Density
Average: 0.8548 g/cm³
Standard Deviation: 0.0003 g/cm³

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Vial Number: 1
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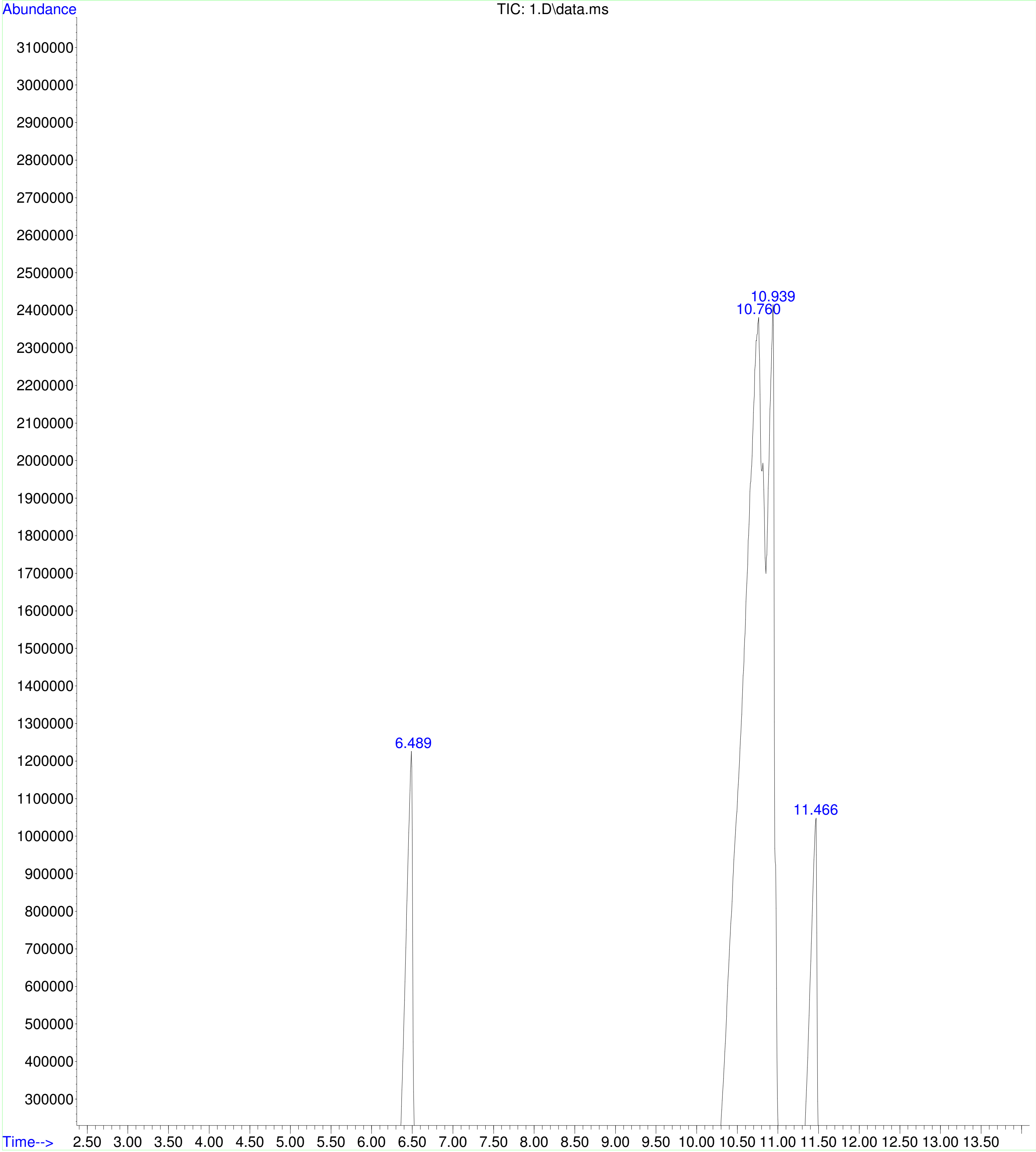

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                 1-Hexadecyne                        73057 000629-74-3 93
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                 9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 86

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                 9-Octadecenoic acid, (E)-          113363 000112-79-8 90

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                 Octadecanoic acid                  114818 000057-11-4 95


FAME RSO.M Mon Jan 09 15:35:30 2012
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Instrument  :    GCMSD
Sample Name: RSO 3
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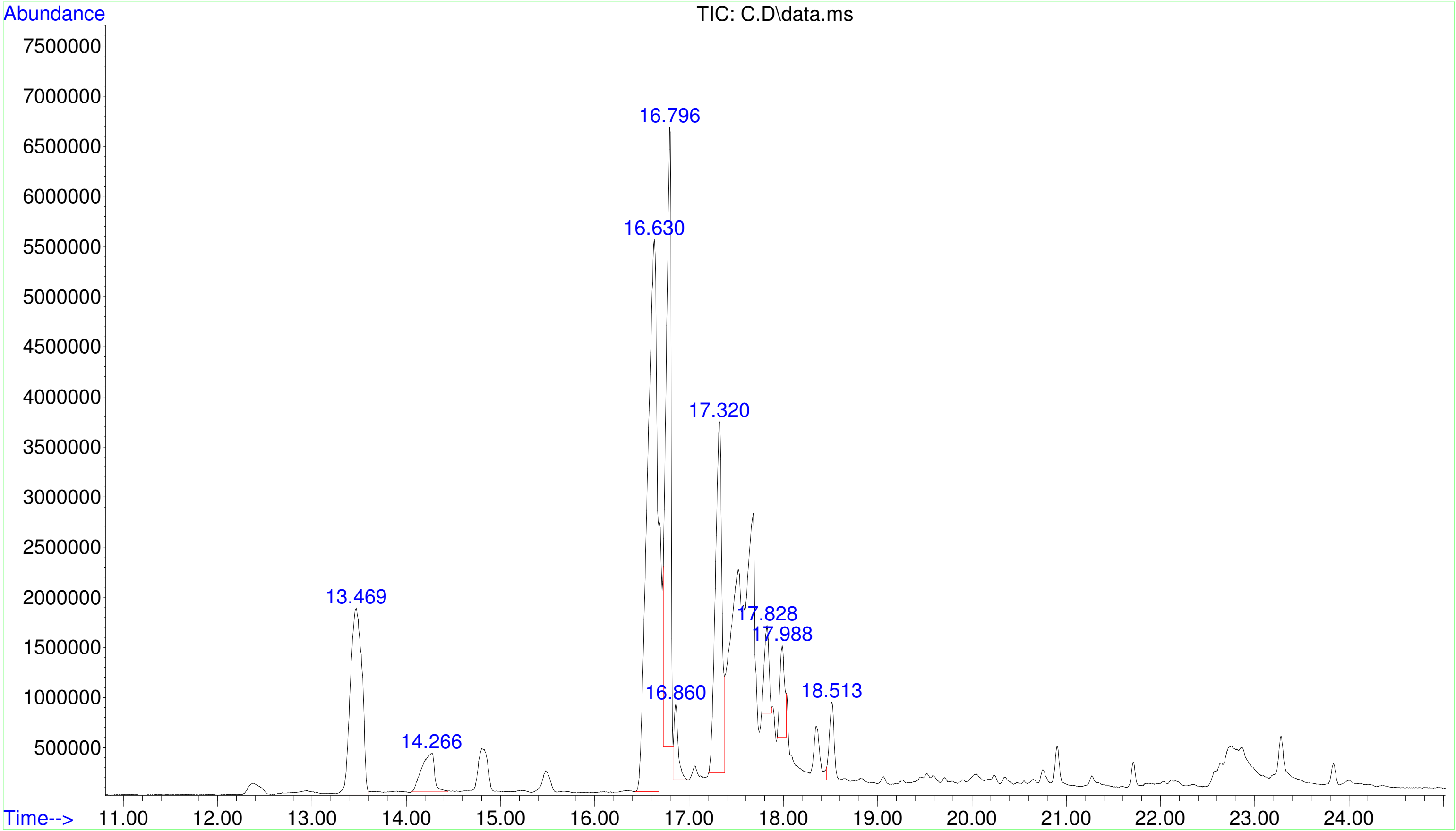

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                                        Library Search Report

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  Operator  : SHAHID
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  Misc      :
  ALS Vial  : 3   Sample Multiplier: 1

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  Integration Events: RTE Integrator - autoint1.e

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                 thyl ester
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                 10,13-Octadecadienoic acid, methyl 121100 056554-62-2 99
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                 methyl ester

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                 7-Octadecenoic acid, methyl ester  122298 057396-98-2 99
                 8-Octadecenoic acid, methyl ester  122297 002345-29-1 99
                 9-Octadecenoic acid, methyl ester  122299 002462-84-2 99

  5  16.860  2.18 C:\Database\NIST05a.L
                 7-Octadecenoic acid, methyl ester  122298 057396-98-2 99
                 8-Octadecenoic acid, methyl ester  122297 002345-29-1 99
                 9-Octadecenoic acid, methyl ester  122299 002462-84-2 99

  6  17.320 15.71 C:\Database\NIST05a.L
                 Octadecanoic acid, methyl ester    123709 000112-61-8 99
                 Heptadecanoic acid, 16-methyl-, me 123732 005129-61-3 98
                 thyl ester
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                 ster
                 Linoleic acid ethyl ester          129812 000544-35-4 98

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                 Octadecanoic acid, ethyl ester     132324 000111-61-5 93
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Vial Number: 1
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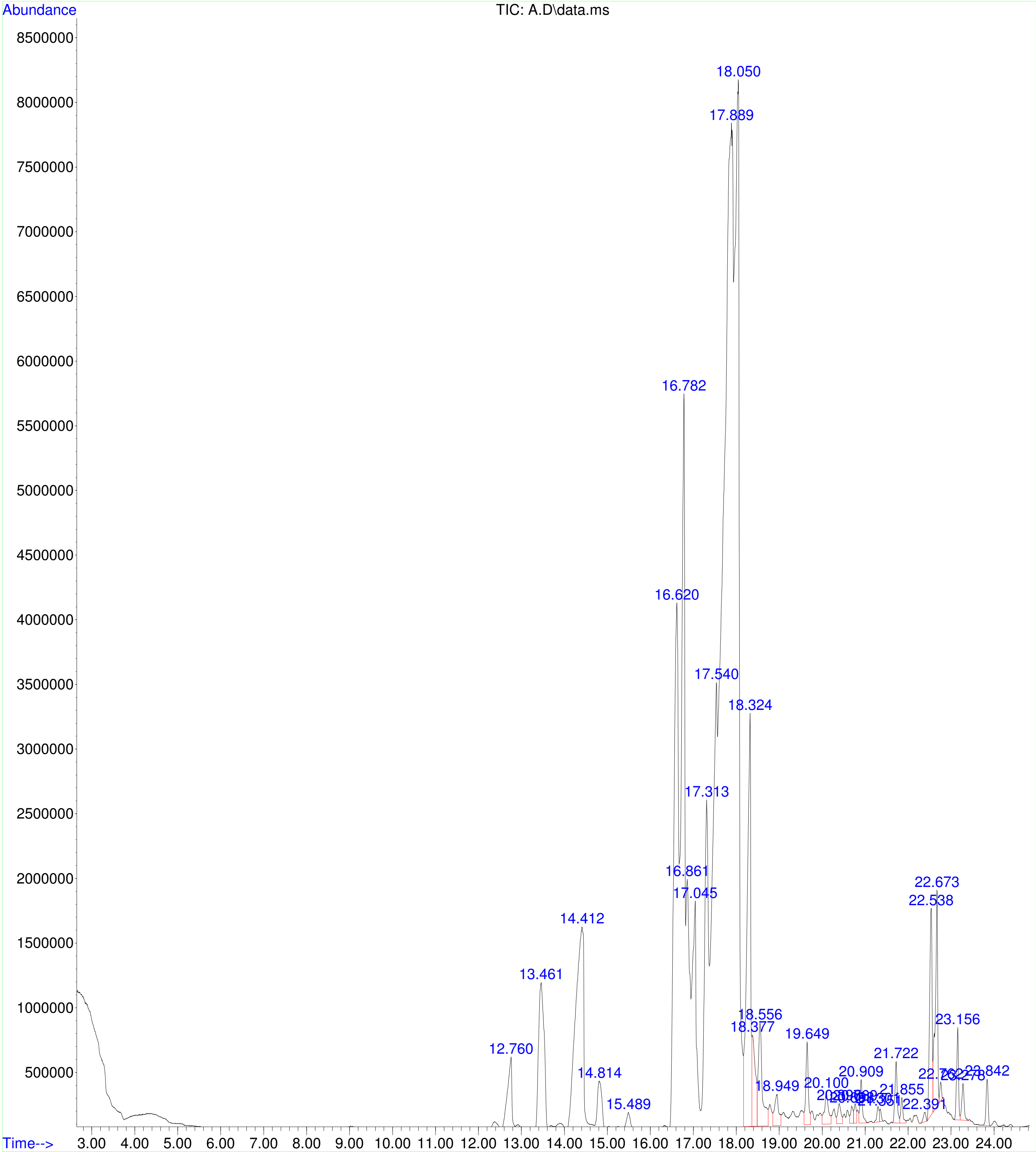

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                                        Library Search Report

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 Data File : A.D
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 Operator  : SHAHID
 Sample    : RSO 1
 Misc      :
 ALS Vial  : 1   Sample Multiplier: 1

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 Integration Events: ChemStation Integrator - autoint1.e

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                 thyl ester
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                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 28

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                 methyl ester
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                 ester

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                 9-Octadecenoic acid, methyl ester, 122326 001937-62-8 99
                  (E)-
                 9-Octadecenoic acid, methyl ester  122299 002462-84-2 99

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                 9,12-Octadecadienoic acid (Z,Z)-   111992 000060-33-3 95
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                thyl ester
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                thyl ester

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                7,11-Hexadecadienal                 82616 1000130-85-7 55
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                ol

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                1,2-15,16-Diepoxyhexadecane         94762 1000192-65-0 86

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                (2-ethylhexyl) ester
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                ooctyl ester
                Phthalic acid, cyclohexylmethyl 2- 143649 1000315-55-5 64
                pentyl ester
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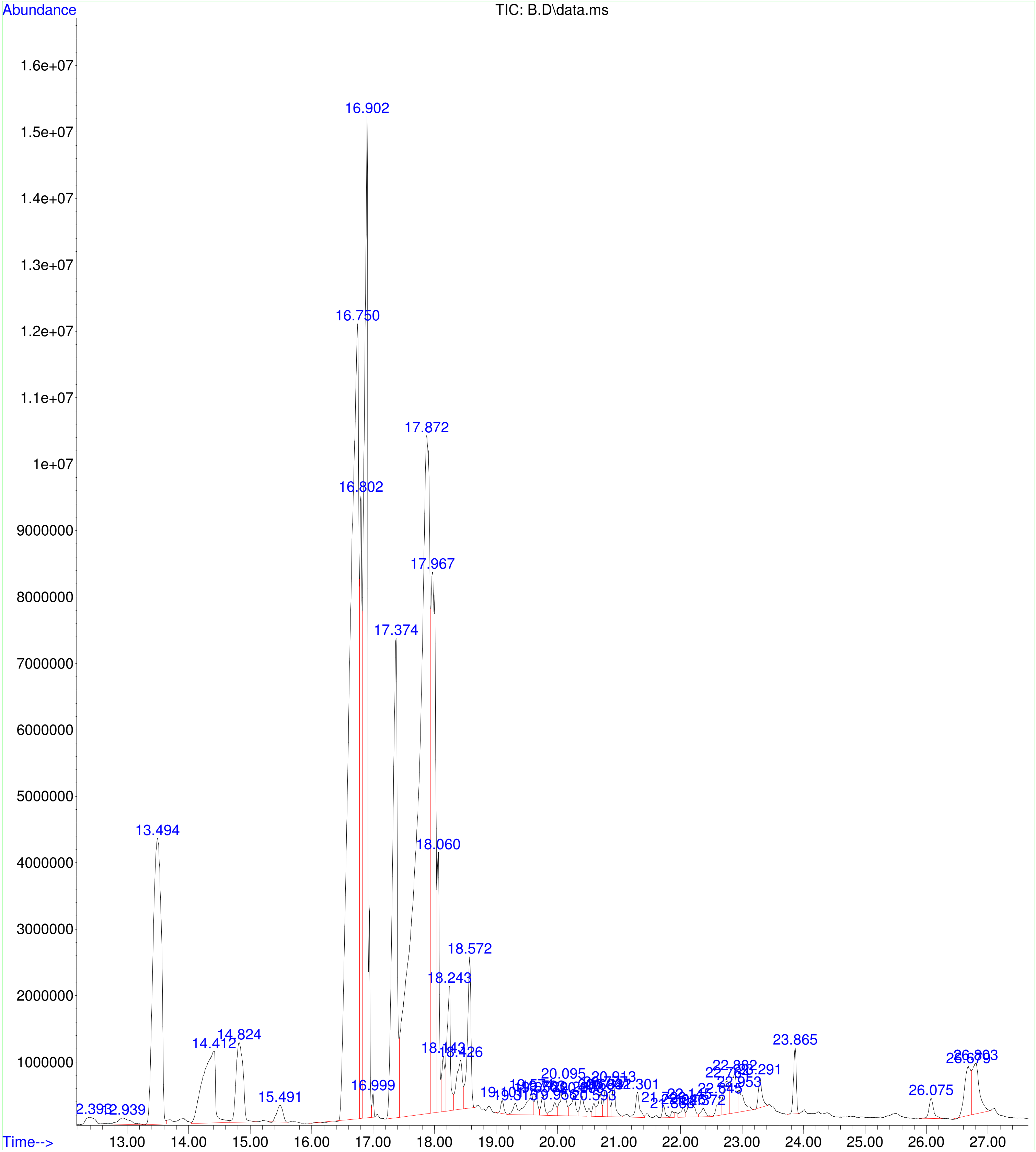

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                 2,4-Decadienal                        24037 002363-88-4 70
                 2,4-Decadienal                        24041 002363-88-4 70
                 2,4-Decadienal, (E,E)-                24067 025152-84-5 64

  2  12.394  0.18 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 80
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 38
                 Cyclohexasiloxane, dodecamethyl-   179152 000540-97-6 35

  3  12.939  0.23 C:\Database\NIST05a.L
                 9-Hexadecenoic acid, methyl ester, 104152 001120-25-8 99
                  (Z)-
                 7-Hexadecenoic acid, methyl ester, 104151 056875-67-3 99
                  (Z)-
                 13-Borabicyclo[7.3.0]tridecane, 13  82546 1000156-41-7 78
                 -propoxy-, (Z)- or (E)-

  4  13.495  6.70 C:\Database\NIST05a.L
                 Hexadecanoic acid, methyl ester    105639 000112-39-0 99
                 Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 96
                 thyl ester
                 Hexadecanoic acid, methyl ester    105644 000112-39-0 95

  5  14.410  2.56 C:\Database\NIST05a.L
                 n-Hexadecanoic acid                 96235 000057-10-3 98
                 n-Hexadecanoic acid                 96234 000057-10-3 98
                 n-Hexadecanoic acid                 96233 000057-10-3 95

  6  14.822  1.56 C:\Database\NIST05a.L
                 Hexadecanoic acid, ethyl ester     114844 000628-97-7 99
                 Ethyl tridecanoate                  86747 028267-29-0 95
                 Tetradecanoic acid, ethyl ester     96268 000124-06-1 95

  7  15.490  0.29 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 58
                 Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 187862 019095-24-0 40
                 11,11,13,13,15,15-hexadecamethyl-
                 Pentasiloxane, dodecamethyl-       166195 000141-63-9 38

  8  16.747 19.89 C:\Database\NIST05a.L
                 10,13-Octadecadienoic acid, methyl 121100 056554-62-2 99
                  ester
                 9,12-Octadecadienoic acid, methyl  121093 002462-85-3 98
                 ester
                 9,12-Octadecadienoic acid (Z,Z)-,  121107 000112-63-0 98
                 methyl ester

  9  16.801  3.88 C:\Database\NIST05a.L
                 9,12,15-Octadecatrienoic acid, met 119875 000301-00-8 99
                 hyl ester, (Z,Z,Z)-
                 9,12,15-Octadecatrienoic acid, met 119876 000301-00-8 99
                 hyl ester, (Z,Z,Z)-
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                9,12,15-Octadecatrienoic acid, met 119877 000301-00-8 97
                hyl ester, (Z,Z,Z)-

10  16.903 11.37 C:\Database\NIST05a.L
                9-Octadecenoic acid, methyl ester, 122326 001937-62-8 99
                 (E)-
                9-Octadecenoic acid (Z)-, methyl e 122323 000112-62-9 99
                ster
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 99

11  16.999  0.11 C:\Database\NIST05a.L
                2H-Pyran-2-one, tetrahydro-6-tride 113389 001227-51-6 72
                cyl-
                2H-Pyran-2-one, tetrahydro-6-propy  19065 000698-76-0 52
                l-
                Dihexadecyl phosphate              186807 002197-63-9 52

12  17.373  6.20 C:\Database\NIST05a.L
                Octadecanoic acid, methyl ester    123709 000112-61-8 99
                Heptadecanoic acid, 16-methyl-, me 123732 005129-61-3 98
                thyl ester
                Octadecanoic acid, methyl ester    123708 000112-61-8 97

13  17.871 23.88 C:\Database\NIST05a.L
                Linoleic acid ethyl ester          129812 000544-35-4 99
                9,12-Octadecadienoic acid, ethyl e 129833 007619-08-1 99
                ster
                9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 94

14  17.967  6.89 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 95
                Oleic Acid                         113354 000112-80-1 94
                9,12,15-Octadecatrienoic acid, eth 128661 001191-41-9 91
                yl ester, (Z,Z,Z)-

15  18.058  1.62 C:\Database\NIST05a.L
                Ethyl Oleate                       131053 000111-62-6 98
                Ethyl Oleate                       131052 000111-62-6 94
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 83

16  18.143  0.43 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 92
                9,12-Octadecadien-1-ol, (Z,Z)-     102837 000506-43-4 90
                9-Oxabicyclo[6.1.0]nonane, cis-     11083 004925-71-7 74

17  18.245  1.30 C:\Database\NIST05a.L
                Octadecanoic acid                  114822 000057-11-4 99
                Octadecanoic acid                  114820 000057-11-4 97
                Octadecanoic acid                  114821 000057-11-4 94

18  18.427  0.81 C:\Database\NIST05a.L
                Isopropyl linoleate                138084 022882-95-7 99
                9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 96
                5-Dodecyne                          33494 019780-12-2 68

19  18.571  1.51 C:\Database\NIST05a.L
                Octadecanoic acid, ethyl ester     132323 000111-61-5 98
                Octadecanoic acid, ethyl ester     132325 000111-61-5 95
                Heptadecanoic acid, 15-methyl-, et 132360 057274-46-1 95
                hyl ester

20  19.101  0.11 C:\Database\NIST05a.L
                Octadecanoic acid                  114821 000057-11-4 64
                Isopropyl stearate                 140303 000112-10-7 38
                Oleic Acid                         113353 000112-80-1 35

21  19.315  0.13 C:\Database\NIST05a.L
                12-Methyl-E,E-2,13-octadecadien-1- 112087 1000130-90-4 90
                ol
                3,6-Octadien-1-ol, 3,7-dimethyl-,   25691 005944-20-7 90
```

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                (Z)-
                2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 87

22  19.572  0.42 C:\Database\NIST05a.L
                1,5-Cyclodecadiene, (E,Z)-          15217 001124-78-3 83
                Bicyclo[6.1.0]non-1-ene              9706 002570-06-1 64
                Cyclododecyne                       32158 001129-90-4 64

23  19.652  0.19 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121113 002566-97-4 90
                ester, (E,E)-
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 90
                ester, (E,E)-
                Cyclohexene, 4-(4-ethylcyclohexyl) 100231 301643-32-3 59
                -1-pentyl-

24  19.764  0.20 C:\Database\NIST05a.L
                2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 90
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 62
                Bicyclo[10.8.0]eicosane, (E)-      110853 1000155-85-0 56

25  19.957  0.16 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 93
                1,5-Cyclodecadiene, (E,Z)-          15218 001124-78-3 92
                Cyclohexanone, 2,2-dimethyl-5-(3-m  44448 141033-65-0 91
                ethyloxiranyl)-, [2.alpha.(R*),3.a
                lpha.]-(.+-.)-

26  20.096  0.49 C:\Database\NIST05a.L
                Cyclopropaneoctanal, 2-octyl-      112082 056196-06-6 95
                (R)-(-)-14-Methyl-8-hexadecyn-1-ol  93525 064566-18-3 92
                Z,Z-10,12-Hexadecadien-1-ol acetat 112002 1000130-89-5 90

27  20.267  0.29 C:\Database\NIST05a.L
                11-Eicosenoic acid, methyl ester   139171 003946-08-5 83
                cis-11-Hexadecenal                  83994 053939-28-9 60
                Z-8-Methyl-9-tetradecenoic acid     85352 1000130-84-5 60

28  20.401  0.24 C:\Database\NIST05a.L
                2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 87
                Bicyclo[10.1.0]tridec-1-ene         41746 054766-91-5 70
                7,11-Hexadecadienal                 82616 1000130-85-7 66

29  20.593  0.11 C:\Database\NIST05a.L
                Cyclopropaneoctanal, 2-octyl-      112082 056196-06-6 90
                13-Octadecenal, (Z)-               102822 058594-45-9 83
                Oleic Acid                         113354 000112-80-1 83

30  20.695  0.24 C:\Database\NIST05a.L
                13-Tetradece-11-yn-1-ol             62946 1000131-00-4 95
                2(1H)-Naphthalenone, octahydro-4a-  62989 054594-42-2 93
                methyl-7-(1-methylethyl)-, (4a.alp
                ha.,7.beta.,8a.beta.)-
                Bicyclo[10.1.0]tridec-1-ene         41746 054766-91-5 93

31  20.775  0.23 C:\Database\NIST05a.L
                Eicosanoic acid, methyl ester      140314 001120-28-1 97
                Eicosanoic acid, methyl ester      140313 001120-28-1 96
                Heptadecanoic acid, methyl ester   114853 001731-92-6 90

32  20.834  0.17 C:\Database\NIST05a.L
                9-Octadecenamide, (Z)-             112657 000301-02-0 78
                9-Octadecenamide, (Z)-             112656 000301-02-0 53
                10-Undecenehydroxamic acid          56421 016791-35-8 38

33  20.914  0.31 C:\Database\NIST05a.L
                Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 72
                Hexasiloxane, tetradecamethyl-     180792 000107-52-8 38
                Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 35
```

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34  21.299  0.28 C:\Database\NIST05a.L
                2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 64
                Bicyclo[10.1.0]tridec-1-ene         41746 054766-91-5 52
                Bicyclo[10.1.0]tridec-1-ene         41747 054766-91-5 46

35  21.727  0.10 C:\Database\NIST05a.L
                Octadecanoic acid, 2-methylpropyl  147957 000646-13-9 86
                ester
                Octadecanoic acid, butyl ester     147942 000123-95-5 46
                Octadecanoic acid, butyl ester     147943 000123-95-5 43

36  21.866  0.05 C:\Database\NIST05a.L
                9-Octadecenoic acid, ethyl ester   131087 006512-99-8 46
                Cyclopropaneoctanal, 2-octyl-      112082 056196-06-6 38
                Hexadecanoic acid, ethyl ester     114847 000628-97-7 38

37  22.048  0.12 C:\Database\NIST05a.L
                Cyclohexene, 4-pentyl-1-(4-propylc 109663 108067-17-0 98
                yclohexyl)-
                Z,Z-10,12-Hexadecadien-1-ol acetat 112002 1000130-89-5 97
                9,12-Octadecadienoyl chloride, (Z, 123598 007459-33-8 90
                Z)-

38  22.144  0.28 C:\Database\NIST05a.L
                2-Methyl-3-(3-methyl-but-2-enyl)-2  72975 1000144-10-2 94
                -(4-methyl-pent-3-enyl)-oxetane
                1H-Cyclopenta[c]furan-1-one, hexah  34739 077384-13-5 50
                ydro-3,6,6-trimethyl-
                2,6,10-Dodecatrien-1-ol, 3,7,11-tr 101443 004128-17-0 45
                imethyl-, acetate, (E,E)-

39  22.374  0.11 C:\Database\NIST05a.L
                2(1H)-Naphthalenone, octahydro-4a-  62989 054594-42-2 95
                methyl-7-(1-methylethyl)-, (4a.alp
                ha.,7.beta.,8a.beta.)-
                2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 94
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 92

40  22.647  0.21 C:\Database\NIST05a.L
                (R)-(-)-14-Methyl-8-hexadecyn-1-ol  93525 064566-18-3 98
                Isopropyl linoleate                138084 022882-95-7 94
                8-Hexadecyne                        73056 019781-86-3 83

41  22.765  0.53 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 96
                Cyclododecyne                       32158 001129-90-4 94
                Cyclohexanecarboxaldehyde, 4-(hydr  19125 092385-32-5 89
                oxymethyl)-

42  22.882  0.63 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 95
                9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 90
                Tridecanedial                       65765 063521-76-6 87

43  22.952  0.35 C:\Database\NIST05a.L
                9-Octadecenal, (Z)-                102821 002423-10-1 93
                Cyclododecyne                       32158 001129-90-4 90
                Bicyclo[10.1.0]tridec-1-ene         41747 054766-91-5 70

44  23.289  0.31 C:\Database\NIST05a.L
                Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 64
                1,1,1,5,7,7,7-Heptamethyl-3,3-bis( 179156 038147-00-1 53
                trimethylsiloxy)tetrasiloxane
                Hexasiloxane, tetradecamethyl-     180792 000107-52-8 47

45  23.866  0.51 C:\Database\NIST05a.L
                1,2-Benzenedicarboxylic acid, mono 110586 004376-20-9 91
                (2-ethylhexyl) ester
                1,2-Benzenedicarboxylic acid, diis 168521 027554-26-3 91
                ooctyl ester
```

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                 1,2-Benzenedicarboxylic acid, dicy 142438 000084-61-7 64
                 clohexyl ester

 46  26.075  0.26 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 50
                 Benzoic acid, 2,5-bis(trimethylsil 161132 003618-20-0 35
                 oxy)-, trimethylsilyl ester
                 Benzoic acid, 2,5-bis(trimethylsil 161131 003618-20-0 35
                 oxy)-, trimethylsilyl ester

 47  26.680  0.88 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid (Z,Z)-,  154542 003443-82-1 96
                 2-hydroxy-1-(hydroxymethyl)ethyl e
                 ster
                 9,12-Octadecadienoic acid (Z,Z)-,  154539 002277-28-3 95
                 2,3-dihydroxypropyl ester
                 9,17-Octadecadienal, (Z)-          101505 056554-35-9 91

 48  26.803  1.01 C:\Database\NIST05a.L
                 9-Octadecenoic acid (Z)-, 2-hydrox 155412 003443-84-3 95
                 y-1-(hydroxymethyl)ethyl ester
                 1H-Indene, 2-butyl-5-hexyloctahydr 101523 055044-33-2 83
                 o-
                 7,10-Hexadecadienoic acid, methyl  102730 016106-03-9 78
                 ester
```

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File        :D:\Data\SHAHID ALI\15nov\C.D
Operator    : SHAHID
Acquired    : 15 Nov 2011  16:57     using AcqMethod FAME RSO.M
Instrument :   GCMSD
Sample Name: RSO 3
Misc Info  :
Vial Number: 3
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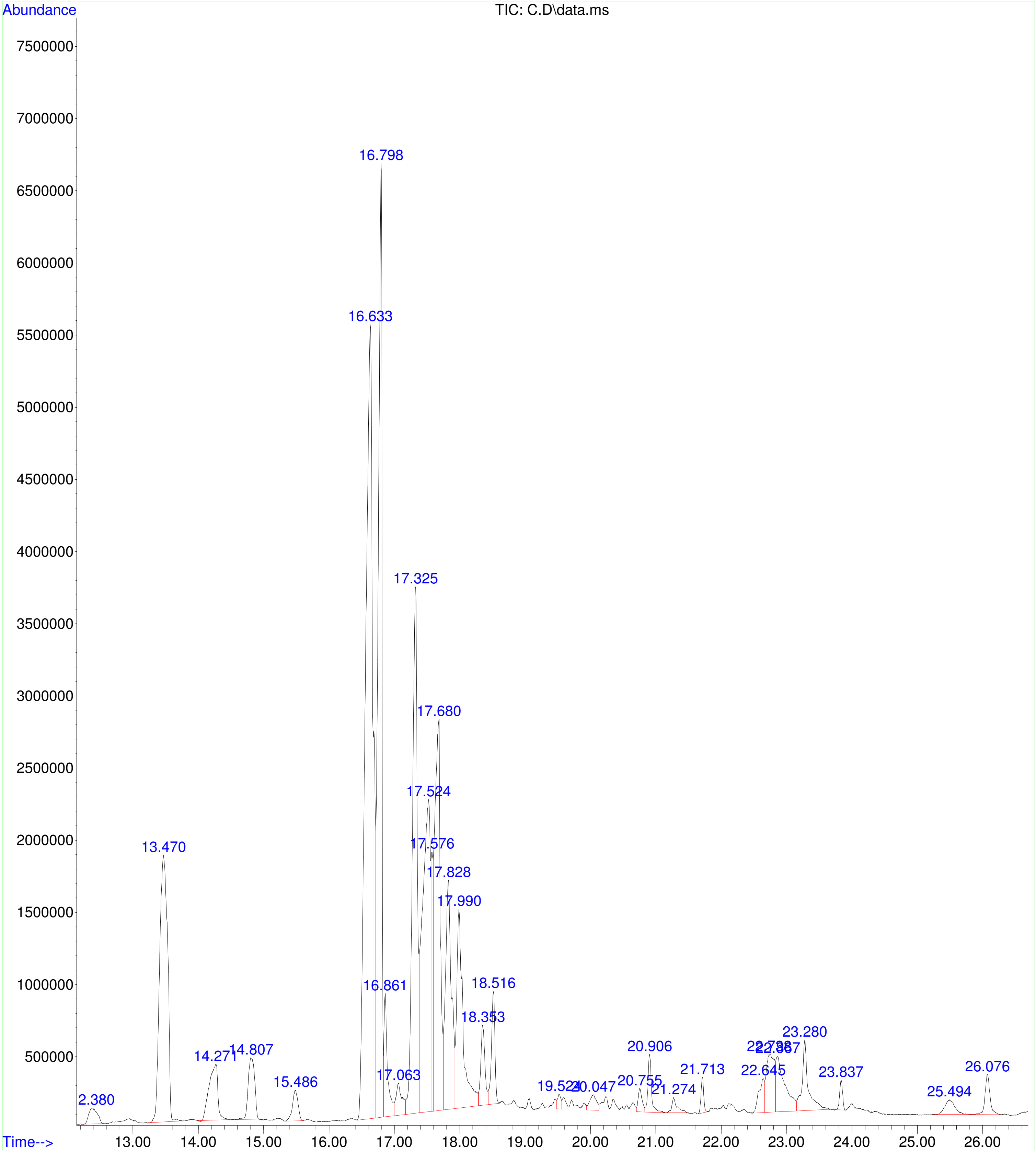

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                                        Library Search Report

  Data Path : D:\Data\SHAHID ALI\15nov\
  Data File : C.D
  Acq On    : 15 Nov 2011  16:57
  Operator  : SHAHID
  Sample    : RSO 3
  Misc      :
  ALS Vial  : 3   Sample Multiplier: 1

  Search Libraries:   C:\Database\NIST05a.L            Minimum Quality:   0

  Unknown Spectrum:   Apex
  Integration Events: ChemStation Integrator - autoint1.e

Pk#     RT  Area%          Library/ID                   Ref#     CAS#   Qual
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  1   2.606  1.86 C:\Database\NIST05a.L
                 2,4-Decadienal, (E,E)-              24069 025152-84-5 90
                 2,4-Decadienal                      24041 002363-88-4 87
                 2,4-Decadienal, (E,E)-              24067 025152-84-5 87

  2   2.654  4.21 C:\Database\NIST05a.L
                 2,4-Decadienal, (E,E)-              24069 025152-84-5 90
                 2,4-Decadienal, (E,E)-              24067 025152-84-5 87
                 2,4-Decadienal                      24041 002363-88-4 87

  3  12.378  0.47 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 64
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 41
                 .beta.-D-Glucopyranosiduronic acid 190556 052092-53-2 25
                 , (5.alpha.,6.alpha.)-7,8-didehydr
                 o-4,5-epoxy-17-methyl-6-[(trimethy
                 lsilyl)oxy]morphinan-3-yl 2,3,4-tr
                 is-O-(trimethylsilyl)-, trimethyls
                 ilyl ester

  4  13.469  7.32 C:\Database\NIST05a.L
                 Hexadecanoic acid, methyl ester    105639 000112-39-0 99
                 Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 97
                 thyl ester
                 Hexadecanoic acid, methyl ester    105644 000112-39-0 96

  5  14.271  1.67 C:\Database\NIST05a.L
                 n-Hexadecanoic acid                 96234 000057-10-3 98
                 n-Hexadecanoic acid                 96235 000057-10-3 95
                 n-Hexadecanoic acid                 96233 000057-10-3 94

  6  14.806  1.40 C:\Database\NIST05a.L
                 Hexadecanoic acid, ethyl ester     114844 000628-97-7 99
                 Hexadecanoic acid, ethyl ester     114847 000628-97-7 94
                 Tetradecanoic acid, ethyl ester     96267 000124-06-1 93

  7  15.485  0.57 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 76
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 50
                 1,1,1,5,7,7,7-Heptamethyl-3,3-bis( 179156 038147-00-1 32
                 trimethylsiloxy)tetrasiloxane

  8  16.635 20.44 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid (Z,Z)-,  121107 000112-63-0 99
                 methyl ester
                 10,13-Octadecadienoic acid, methyl 121100 056554-62-2 99
                  ester
                 9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 99
                 methyl ester

  9  16.796 12.45 C:\Database\NIST05a.L
                 7-Octadecenoic acid, methyl ester  122298 057396-98-2 99
                 8-Octadecenoic acid, methyl ester  122297 002345-29-1 99
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                9-Octadecenoic acid, methyl ester  122299 002462-84-2 99

10  16.860  1.53 C:\Database\NIST05a.L
                7-Octadecenoic acid, methyl ester  122298 057396-98-2 99
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 99
                9-Octadecenoic acid, methyl ester  122299 002462-84-2 99

11  17.063  0.68 C:\Database\NIST05a.L
                Oleic Acid                         113353 000112-80-1 96
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 96
                9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 95

12  17.325  8.70 C:\Database\NIST05a.L
                Octadecanoic acid, methyl ester    123709 000112-61-8 99
                Heptadecanoic acid, 16-methyl-, me 123732 005129-61-3 98
                thyl ester
                Octadecanoic acid, methyl ester    123708 000112-61-8 97

13  17.523  8.47 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 92
                2-Chloroethyl linoleate            148820 025525-76-2 87
                9,12-Octadecadienoic acid (Z,Z)-   111992 000060-33-3 86

14  17.577  1.57 C:\Database\NIST05a.L
                13-Tetradece-11-yn-1-ol             62946 1000131-00-4 91
                9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 91
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 80

15  17.678  7.84 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 97
                Oleic Acid                         113353 000112-80-1 90
                6-Octadecenoic acid, (Z)-          113359 000593-39-5 87

16  17.828  4.79 C:\Database\NIST05a.L
                Linoleic acid ethyl ester          129811 000544-35-4 99
                9,12-Octadecadienoic acid, ethyl e 129833 007619-08-1 99
                ster
                Linoleic acid ethyl ester          129812 000544-35-4 98

17  17.988  4.38 C:\Database\NIST05a.L
                Ethyl Oleate                       131053 000111-62-6 89
                9-Octadecenoic acid, ethyl ester   131087 006512-99-8 83
                Ethyl Oleate                       131052 000111-62-6 80

18  18.352  1.15 C:\Database\NIST05a.L
                Benzeneethanamine, N-[(pentafluoro 187434 055429-13-5 27
                phenyl)methylene]-.beta.,3,4-tris[
                (trimethylsilyl)oxy]-
                3,4-Dihydroxymandelic acid, ethyl  176762 1000071-70-2 27
                ester, tri-TMS
                Terbutaline, N-trifluoroacetyl-o,o 186415 325836-92-8 27
                ,o-tris(trimethylsilyl)deriv.

19  18.518  1.36 C:\Database\NIST05a.L
                Octadecanoic acid, ethyl ester     132325 000111-61-5 96
                Octadecanoic acid, ethyl ester     132323 000111-61-5 96
                Octadecanoic acid, ethyl ester     132324 000111-61-5 94

20  19.523  0.17 C:\Database\NIST05a.L
                Bicyclo[6.1.0]non-1-ene              9706 002570-06-1 60
                1,5-Cyclodecadiene, (E,Z)-          15217 001124-78-3 49
                2-Methyl-3-(3-methyl-but-2-enyl)-2  72975 1000144-10-2 49
                -(4-methyl-pent-3-enyl)-oxetane

21  20.048  0.36 C:\Database\NIST05a.L
                Cyclopropaneoctanal, 2-octyl-      112082 056196-06-6 98
                Z,Z-10,12-Hexadecadien-1-ol acetat 112002 1000130-89-5 90
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 90
                ester, (E,E)-
```

```
 22  20.754  0.32 C:\Database\NIST05a.L
                 Eicosanoic acid, methyl ester      140314 001120-28-1 97
                 Eicosanoic acid, methyl ester      140313 001120-28-1 95
                 Nonadecanoic acid, 11-methyl-, met 140336 055334-33-3 87
                 hyl ester

 23  20.909  0.70 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 80
                 6,8-Dichloro-2-[4-chlorophenyl]-4- 176646 1000255-89-2 56
                 bromoacetylquinoline
                 Benzoic acid, 2,4-bis[(trimethylsi 161138 010586-16-0 35
                 lyl)oxy]-, trimethylsilyl ester

 24  21.272  0.27 C:\Database\NIST05a.L
                 12-Methyl-E,E-2,13-octadecadien-1- 112087 1000130-90-4 83
                 ol
                 2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 78
                 E,E-10,12-Hexadecadien-1-ol acetat 112004 1000130-87-6 49

 25  21.711  0.33 C:\Database\NIST05a.L
                 Octadecanoic acid, butyl ester     147942 000123-95-5 93
                 Octadecanoic acid, butyl ester     147943 000123-95-5 83
                 Octadecanoic acid, 2-methylpropyl  147957 000646-13-9 78
                 ester

 26  22.647  0.62 C:\Database\NIST05a.L
                 6-Tetradecyne                       52900 003730-08-3 92
                 cis,cis,cis-7,10,13-Hexadecatriena  81217 056797-43-4 80
                 7-Tetradecyne                       52908 035216-11-6 78

 27  22.738  1.60 C:\Database\NIST05a.L
                 9,17-Octadecadienal, (Z)-          101505 056554-35-9 95
                 Bicyclo[10.1.0]tridec-1-ene         41746 054766-91-5 83
                 2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 80

 28  22.866  1.77 C:\Database\NIST05a.L
                 2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 94
                 Cyclododecyne                       32158 001129-90-4 92
                 9,17-Octadecadienal, (Z)-          101505 056554-35-9 91

 29  23.278  1.51 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 72
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 62
                 1,1,1,5,7,7,7-Heptamethyl-3,3-bis( 179156 038147-00-1 50
                 trimethylsiloxy)tetrasiloxane

 30  23.834  0.30 C:\Database\NIST05a.L
                 1,2-Benzenedicarboxylic acid, mono 110586 004376-20-9 91
                 (2-ethylhexyl) ester
                 4-Methoxyanthranilic acid           34368 004294-95-5 64
                 1,2-Benzenedicarboxylic acid, dicy 142440 000084-61-7 64
                 clohexyl ester

 31  25.493  0.51 C:\Database\NIST05a.L
                 Cyclononasiloxane, octadecamethyl- 189576 000556-71-8 59
                 1,1,1,5,7,7,7-Heptamethyl-3,3-bis( 179156 038147-00-1 42
                 trimethylsiloxy)tetrasiloxane
                 Silane, [[4-[1,2-bis[(trimethylsil 180821 056114-62-6 32
                 yl)oxy]ethyl]-1,2-phenylene]bis(ox
                 y)]bis[trimethyl-

 32  26.076  0.69 C:\Database\NIST05a.L
                 Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 187862 019095-24-0 32
                 11,11,13,13,15,15-hexadecamethyl-
                 N-Benzyl-N-ethyl-p-isopropylbenzam 112663 015089-22-2 25
                 ide
                 Cyclononasiloxane, octadecamethyl- 189575 000556-71-8 25
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File        :D:\Data\CITRA\4.D
Operator    : WANI
Acquired    :  5 Aug 2011   9:00     using AcqMethod FAME.M
Instrument :   GCMSD
Sample Name: 4
Misc Info  :
Vial Number: 4
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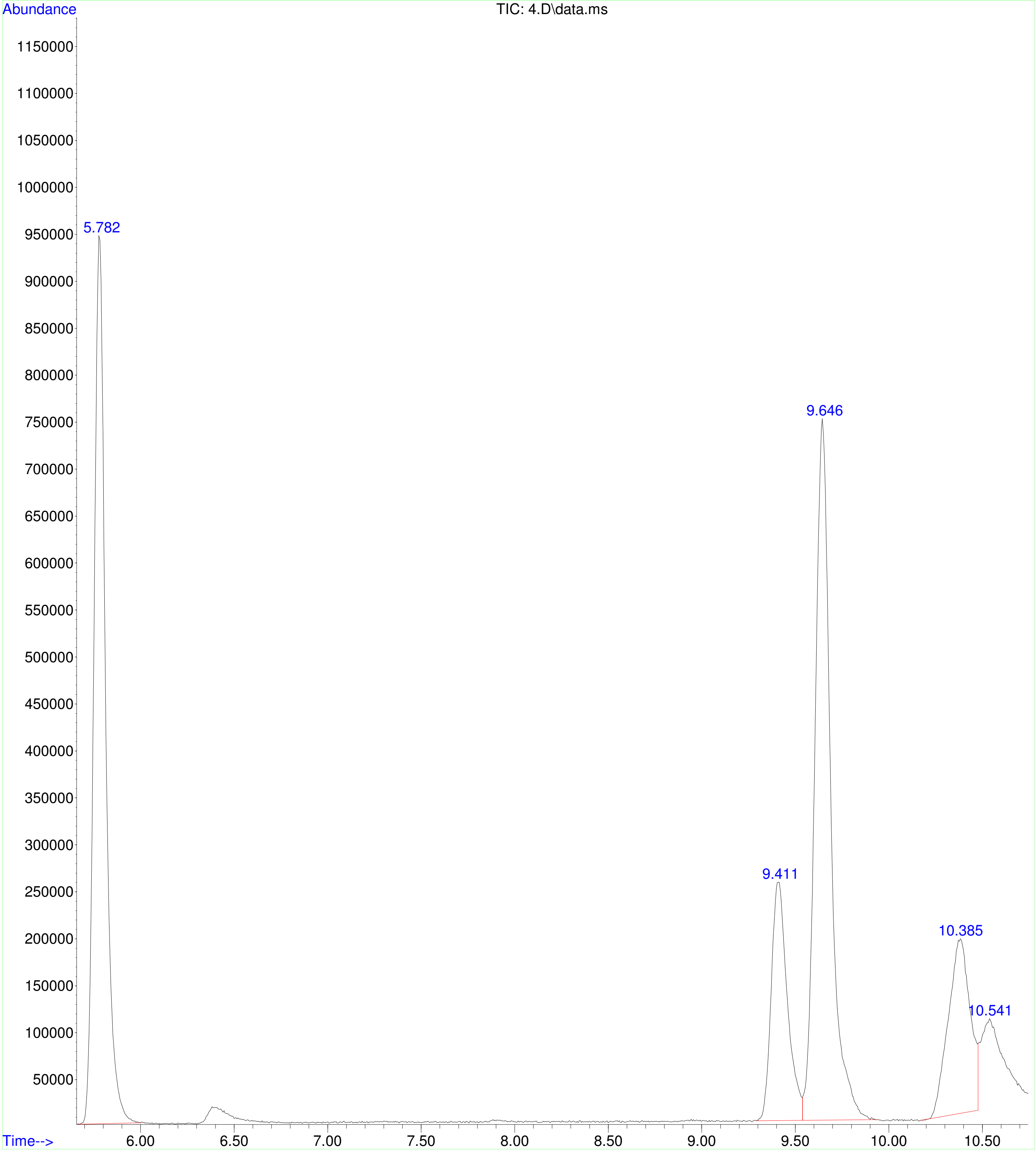

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                                        Library Search Report

  Data Path : D:\Data\CITRA\
  Data File : 4.D
  Acq On    :  5 Aug 2011   9:00
  Operator  : WANI
  Sample    : 4
  Misc      :
  ALS Vial  : 4   Sample Multiplier: 1

  Search Libraries:   C:\Database\NIST05a.L            Minimum Quality:   0

  Unknown Spectrum:   Apex
  Integration Events: ChemStation Integrator - autoint1.e

Pk#     RT  Area%          Library/ID                 Ref#     CAS#   Qual
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  1   5.783 32.97 C:\Database\NIST05a.L
                 Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 97
                 thyl ester
                 Hexadecanoic acid, methyl ester    105639 000112-39-0 96
                 Hexadecanoic acid, methyl ester    105644 000112-39-0 96

  2   9.409 12.37 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 99
                 methyl ester
                 9,12-Octadecadienoic acid (Z,Z)-,  121107 000112-63-0 99
                 methyl ester
                 8,11-Octadecadienoic acid, methyl  121095 056599-58-7 99
                 ester

  3   9.645 35.56 C:\Database\NIST05a.L
                 8-Octadecenoic acid, methyl ester  122297 002345-29-1 99
                 11-Octadecenoic acid, methyl ester 122331 001937-63-9 99
                 , (Z)-
                 9-Octadecenoic acid, methyl ester, 122326 001937-62-8 99
                  (E)-

  4  10.383 12.25 C:\Database\NIST05a.L
                 Octadecanoic acid, methyl ester    123709 000112-61-8 99
                 Heptadecanoic acid, 16-methyl-, me 123732 005129-61-3 98
                 thyl ester
                 Octadecanoic acid, methyl ester    123708 000112-61-8 97

  5  10.543  6.84 C:\Database\NIST05a.L
                 1,9-Tetradecadiene                  52915 112929-06-3 91
                 9,12-Octadecadienoic acid (Z,Z)-   111992 000060-33-3 91
                 9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 64


FAME RSO.M Mon Jan 09 15:38:11 2012
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```
File        :D:\Data\SHAHID ALI\15nov\A.D
Operator    : SHAHID
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Instrument  :    GCMSD
Sample Name: RSO 1
Misc Info   :
Vial Number: 1
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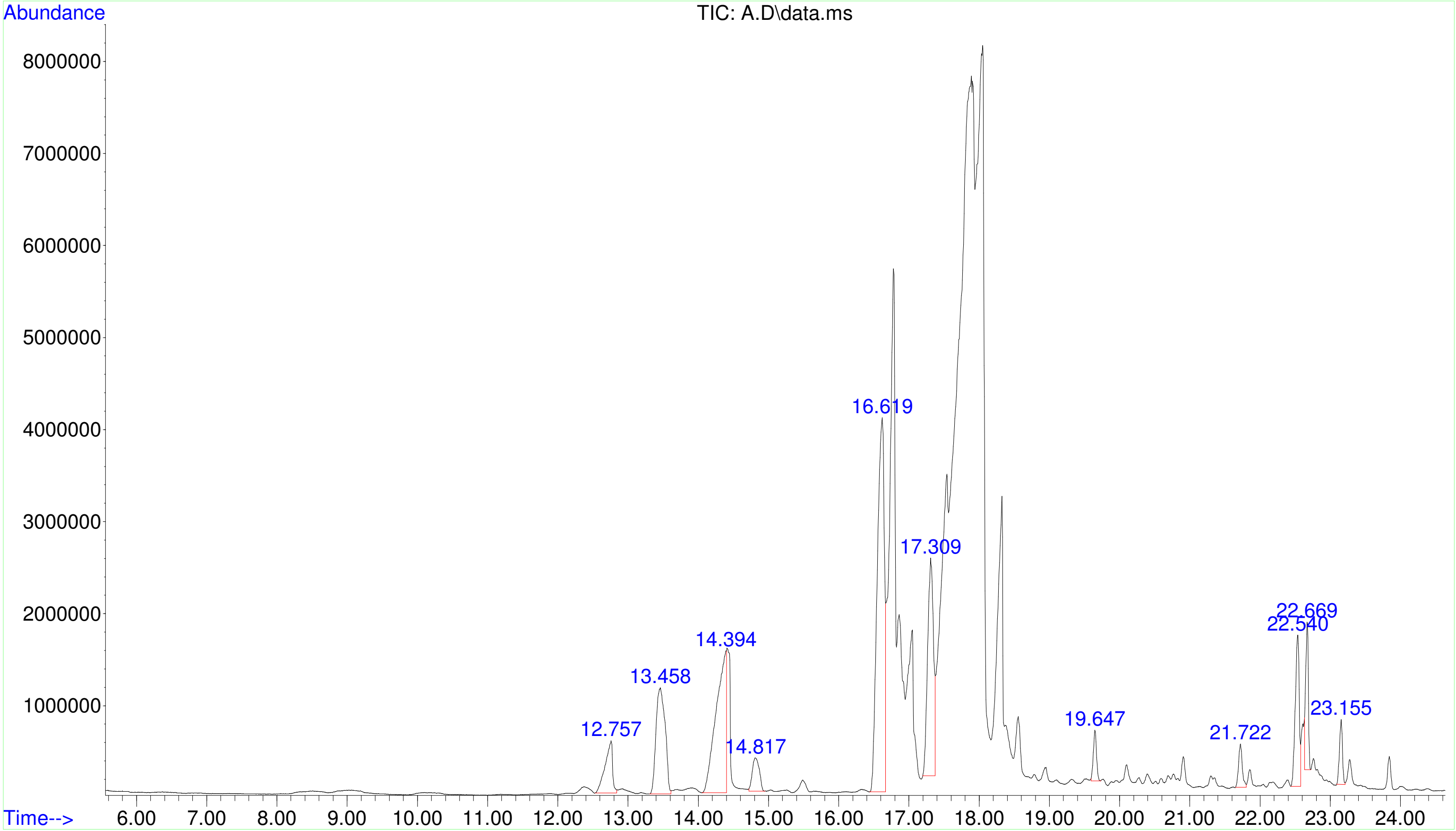

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                                        Library Search Report

  Data Path : D:\Data\SHAHID ALI\15nov\
  Data File : A.D
  Acq On    : 15 Nov 2011  15:47
  Operator  : SHAHID
  Sample    : RSO 1
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

  Search Libraries:   C:\Database\NIST05a.L            Minimum Quality:   0

  Unknown Spectrum:   Apex
  Integration Events: RTE Integrator - autoint1.e

Pk#     RT  Area%          Library/ID                   Ref#     CAS#   Qual
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                 n-Hexadecanoic acid                  96235 000057-10-3 98
                 n-Hexadecanoic acid                  96233 000057-10-3 98
                 n-Hexadecanoic acid                  96234 000057-10-3 97

  2  13.458 11.44 C:\Database\NIST05a.L
                 Hexadecanoic acid, methyl ester    105639 000112-39-0 99
                 Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 98
                 thyl ester
                 Hexadecanoic acid, methyl ester    105644 000112-39-0 96

  3  14.394 16.74 C:\Database\NIST05a.L
                 n-Hexadecanoic acid                  96235 000057-10-3 98
                 n-Hexadecanoic acid                  96234 000057-10-3 97
                 n-Hexadecanoic acid                  96233 000057-10-3 96

  4  14.817  2.75 C:\Database\NIST05a.L
                 Hexadecanoic acid, ethyl ester     114844 000628-97-7 98
                 Hexadecanoic acid, ethyl ester     114848 000628-97-7 91
                 Tetradecanoic acid, ethyl ester     96268 000124-06-1 83

  5  16.619 31.40 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid (Z,Z)-,  121107 000112-63-0 99
                 methyl ester
                 9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 99
                 methyl ester
                 9,12-Octadecadienoic acid, methyl  121093 002462-85-3 99
                 ester

  6  17.309 15.19 C:\Database\NIST05a.L
                 Octadecanoic acid, methyl ester    123709 000112-61-8 99
                 Octadecanoic acid, methyl ester    123708 000112-61-8 97
                 Octadecanoic acid, methyl ester    123700 000112-61-8 96

  7  19.647  1.91 C:\Database\NIST05a.L
                 Heptafluorobutanoic acid, heptadec 180157 1000282-97-3 15
                 yl ester
                 Oxalic acid, monoamide, N-(2-octyl  96747 1000309-47-3 15
                 )-, isobutyl ester
                 Carbonic acid, isobutyl octadecyl  161481 1000314-61-5 11
                 ester

  8  21.722  1.88 C:\Database\NIST05a.L
                 Octadecanoic acid, 2-methylpropyl  147957 000646-13-9 94
                 ester
                 Octadecanoic acid, butyl ester     147942 000123-95-5 90
                 Octadecanoic acid, butyl ester     147943 000123-95-5 90

  9  22.540  7.20 C:\Database\NIST05a.L
                 Cyclododecyne                        32158 001129-90-4 90
                 Isopropyl linoleate                 138084 022882-95-7 81
                 5-Tetradecyne                        52902 060212-34-2 70
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```
 10  22.669  4.72 C:\Database\NIST05a.L
                 9-Octadecenal, (Z)-                102821 002423-10-1 95
                 9,17-Octadecadienal, (Z)-          101505 056554-35-9 87
                 2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 60

 11  23.155  2.23 C:\Database\NIST05a.L
                 2-Propenoic acid, 3-(dimethylamino  12489 000999-59-7 35
                 )-, methyl ester
                 Myristoyl chloride                  89240 000112-64-1 30
                 4-Cyclopropylmethylbenzonitrile     27994 161894-17-3 30
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