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PRODUCTION OF BIO-FUEL: EFFECT OF THE ADDITION OF CO-SOLVENT (CO_2) IN THE NON-CATALYTIC TRANSESTERIFICATION SUPERCRITICAL METHANOL TOWARDS OPERATING CODITIONS

(PENGHASILAN *BIO-FUEL: KESAN PENAMBAHAN KARBON DIOKSIDA (CO2) DI DALAM PROSES KRITIKAL TRANSESTERIFIKASI METANOL TANPA KATALIS TERHADAP KEADAAN OPERASI)*

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ABSTRACT

This research focused on effect of co-solvent towards production of biodiesel via sub/supercritical methanol. The objective of this research is to study the effect of CO_2 as co-solvent in production of Jatropha Oil Methyl Ester at sub/Supercritical of methanol and to optimize operating parameters such as reaction temperature, CO_2 volume and the ratio of methanol/oil. The reaction has been carried out in the absence of catalyst due to the easier purification process. The raw materials used in this study are refined jatropha oil, high grade methanol (solvent) and CO_2 (co-solvent). It is believed that addition of co-solvent with lower critical point will reduce the severity of reaction temperature and pressure. Jatropha oil, methanol and CO_2 were charged into the supercritical reactor with appropriate mole ratio. The mixture is then heated up to desired reaction temperature. The reaction pressure was recorded and the reactor is cooling down until room temperature. The product is then removed and proceeds for purification. The product sample is analyzed to determine the yield percentage of methyl ester using gas chromatography. The duration for reaction was fixed at 5 minutes. The reaction temperature was varied at 160°C to 300°C. CO_2 is added into reaction system and act as co-solvent in order to decrease the pressure. The amount of CO_2 added is measured in terms of volumes, which are at 0.018 m^3, 0.055 m^3 and 0.092 m^3, respectively. Result shows that, addition of CO_2 in the reaction system manage to decrease the reaction pressure. The best volume of CO_2 addition obtained from this study was 0.018 m^3 with reaction pressure 15.1 MPa and yields 85.45 w/w% of jatropha oil methyl ester (JOME) at reaction temperature of 300°C. This study shows that, the addition of CO_2 as co-solvent is a promising method to reduce the reaction pressure and acceptable for future studies.

ABSTRAK

Fokus kajian ini ialah terhadap kesan larutan sampingan ke atas penghasilan biodiesel pada bawah tahap genting dan atas tahap genting methanol. Objektif penyelidikan ini adalah untuk mengkaji kesan larutan sampingan dalam penghasilan Minyak Jatropha Metil Ester (JOME) pada bawah tahap genting dan atas tahap genting methanol dan tahap optima pemboleh ubah seperti suhu tindak balas, isipadu karbon dioksida dan nisbah mol minyak/alkohol. Tindak balas telah dijalankan tanpa kehadiran pemangkin untuk memudahkan proses penulenan . Bahan mentah yang digunakan dalam kajian ini adalah minyak jatropha, metanol berkualiti tinggi sebagai pelarut, dan karbon dioksida sebagai pelarut sampingan. Dipercayai bahawa dengan penambahan pelarut sampingan yang mempunyai tahap genting yang lebih rendah dapat mengurangkan keparahan suhu dan tekanan tindak balas. Minyak jatropha, metanol dan karbon dioksida dimasukkan ke dalam penindak balas mengikut nisbah yang di tetapkan. Campuran itu tadi di panaskan sehingga mencapai suhu tindak balas yang di kehendaki dan apabila tindak balas lengkap, tekanan tindak balas direkodkan serta di sejukkan ke suhu bilik. Produk di keluarkan untuk proses penulenan dan contoh produk di analisis menggunakan kromatografi gas untuk menentukan jumlah peratusan metil ester. Jangka masa tindak balas di tetapkan pada 5 minit. Suhu tindak balas telah di variasi kan dari $160^{O}C$ kepada $300^{O}C$. Karbon dioksida telah di masukkan ke dalam sistem dan bertindak sebagai larutan sampingan untuk mengurangkan tekanan. Jumlah karbon dioksida yang di masukkan di sukat dalam unit isipadu, iaitu pada 0.018 m^3, 0.055 m^3 dan 0.092 m^3, masing- masing. Berdasarkan keputusan yang di perolehi, penambahan karbon dioksida ke dalam tindak balas dapat mengurangkan tekanan semasa tindak balas. Isipadu terbaik yang di perolehi berdasarkan kajian ialah ialah 0.018 m^3 dengan tekanan dalam tindak balas 15.1MPa dan hasil JOME ialah 85.45 w/w % pada suhu tindak balas $300^{o}C$. Kajian ini menunjukkan, penambahan larutan sampingan adalah kaedah yang menjanjikan penurunan tekanan tindak balas dan boleh di guna pakai untuk kajian pada masa hadapan.

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ASTM	American Society for Testing and Materials
EPA	Environmental Protection Agency
FAME	Fatty Acid Methyl Ester
GL	Glycerin
SCM	Supercritical Methanol
T_{CA}	Critical Temperature of species A
T_{CB}	Critical Temperature of species B
TG	Triglyceride

CHAPTER 1

INTRODUCTION

1.1 Background of Study

A supercritical condition is a condition when a substance at temperature and pressure above its critical point. The supercritical fluid at supercritical condition can diffuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Carbon dioxide and water are the most commonly used as supercritical fluids (Supercritical fluid 2009).

In addition, there is no surface tension in a supercritical condition, as there is no liquid or gas phase boundary. By changing the pressure and temperature of the fluid, the properties can be “tuned” to be more liquid- or more gas-like. One of the most important properties is the solubility of material in the fluid. Solubility in a supercritical fluid tends to increase with density of the fluid (at constant temperature). Since density increases with pressure, solubility tends to increase with pressure. The relationship with temperature is a little more complicated. At constant density, solubility will increase with temperature. However, close to the critical point, the density can drop sharply with a slight increase in temperature. Therefore, close to the critical temperature, solubility often drops with increasing temperature, and then rises again (Supercritical fluid 2009).

All supercritical fluids are completely miscible with each other so for a mixture a single phase can be guaranteed if the critical point of the mixture is exceeded. The critical point of a binary mixture can be estimated as the arithmetic mean of the critical temperatures and pressures of the two components (Supercritical Fluid 2009)

$$T_{C(mix)} = (\text{mole fraction A}) \times T_{CA} + (\text{mole fraction B}) \times T_{CB}. \qquad (1)$$

For greater accuracy, the critical point can be calculated using equations of state, such as the Peng Robinson, or group contribution methods. Other properties, such as density, can also be calculated using equations of state. Any commercialization of a process that uses supercritical condition must involve a cost analysis that should indicate that the advantages in the new process offset the penalty of high pressure operations. A variety of supercritical condition processes have been commercialized (Supercritical Fluid 2009).

Many other processes have been investigated on a lab or pilot plant scale and have the potential to be scaled up in the near future. Supercritical condition widely used in supercritical fluid chromatography, fractionation, reaction, applications in the material and polymer industry, food applications, pharmaceutical application and environmental application .Another application of fluid highlighted in this research is the transesterification. Transesterification is one of the important processes in the production of biodiesel.

1.2 Problem Statement

Supercritical methanol is believed to solve problems associated with the two phase nature of normal methanol/oil mixtures in transesterification reaction by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. However, methanol/oil are alone in the production required temperatures of 350-400°C and pressure of 45-65MPa, which are not viable in practice in industry (Cao et al.)

The purpose of this research is to study the effect of CO2 at different volume in production of methyl ester using lab scale high pressure reactor (batch mode). It is believed that, with CO2 as co-solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction (Cao et al.)

1.3 Objectives of Research

The objectives of this project are:

- To study the effect of CO_2 on sub/supercritical methanol.
- To optimize operating parameters such as reaction temperature, CO_2 volume and the ratio of methanol/oil

1.4 Scope of Research

This research is conducted to study the effect of co-solvent added in the production of Jatropha Oil Methyl Ester at subcritical and supercritical condition. In order to reach subcritical and supercritical condition in the process, the reaction temperature is fixed at range of 160°C to 300°C .The significant of the range is due to the sub/supercritical point of methanol as solvent.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Transesterification of triglycerides are in oils is not a new process. Scientists E. Duffy and J. Patrick conducted it as early as 1853. The name 'biodiesel' has been given to transesterified vegetable oil to describe its use as a diesel fuel (Demirbas 2005).

Vegetable oils have not been accepted as a diesel engine fuel based on two reasons. They are more expensive than petroleum fuels and they are too viscous to be atomized efficiently in a diesel engine. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines. However, a need exists to find away to reduce their viscosity. Conversion of oil to its corresponding fatty ester appears to be the most promising solution to the high viscosity problem. The molecular weight is reduced to almost one third its value by esterification with subsequent marked reduction in viscosity (S. Hawash,2009)

2.2 Biodiesel

Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Biodiesel is produced from any fat or oil such as soybean oil, through a refinery process called transesterification. This process is a reaction of the oil with an alcohol to remove the glycerin, which is a by-product of biodiesel production (Board, 2010).

Fuel-grade biodiesel must be produced to strict industry specifications of American Society for Testing and Materials (ASTM D6751) in order to insure proper performance. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D6751 specifications for use in diesel engines. The National Biodiesel Board has released the following production volume estimates for the US (Board, 2010)

Table 2.1: Production of biodiesel in US

Year	**Production of biodiesel, million gallons**
2008	700
2007	450
2006	250
2005	75
2004	25
2003	20
2002	15

Sources: National Biodiesel Board 2010

It is clearly shows that the demand for biodiesel is increasing in US. However, this phenomenon also happens to other country all over the world. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the Clean Air Act. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel. In addition, the exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel (Board, 2010).

Of the major exhaust pollutants, both unburned hydrocarbons and nitrogen oxides are ozone or smog forming precursors. The use of biodiesel results in a substantial reduction of unburned hydrocarbons. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the most stringent emissions testing protocols required by Environmental Protection Agency (EPA) for certification of fuels or fuel additives in the US, the overall ozone forming potential of the speciated hydrocarbon emissions from biodiesel was nearly 50 percent less than that measured for diesel fuel (Board, 2010).

2.3 Sources of Biodiesel

Vegetable oils and animal fat are two common feedstock used for biodiesel. However, vegetable oils are mostly used as the feedstock of biodiesel due to it is renewable sources such as soybean oil, corn oil, palm oil, jatropha oil, algae, cooking oil, seaweed, sunflower and sugarcane. However, the most popular vegetable oils for biodiesel feedstock are palm oil and algae.

2.3.1 Biodiesel from Algae

Algae have emerged as one of the most promising sources for biodiesel production. The current oil crises and fast depleting fossil oil reserves have made it more imperative for organizations and countries to invest more time and efforts into research on suitable renewable feedstock such as algae. An alga (singular alga) is a term that encompasses many different groups of living organisms. Algae capture light energy through photosynthesis and convert inorganic substances into simple sugars using the captured energy (Castoroil 2006).

Algae are usually found in damp places or bodies of water and thus are common in terrestrial as well as aquatic environments. However, terrestrial algae are usually rather inconspicuous and far more common in moist, tropical regions than dry ones, because algae lack vascular tissues and other adaptions to live on land. As mentioned above, algae grow in almost every habitat in every part of the world (Castoroil 2006). However, the production of biodiesel from algae is not practical for industry in Malaysia as the weather here is not constantly moist. Thus, algae are not a suitable feedstock for biodiesel in dry country such as in Malaysia.

2.3.2 Biodiesel from Palm Oil

Palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids, about 50% and 80%, respectively. The oil palm gives its name to the 16-carbon saturated fatty acid palmitic acid found in palm oil; monounsaturated oleic acid is also a constituent of palm oil while palm kernel oil contains mainly lauric acid (Palm Oil 2010).

Palm is also used to make biodiesel, as either a simply-processed palm oil mixed with petro diesel, or processed through transesterification to create a palm oil methyl ester blend, which meets the international biodiesel standards (EN 14214) specification, with glycerin as a byproduct. The actual process used varies between countries, and the requirements of different export markets. Next-generation biofuel production processes are also being tested in relatively small trial quantities. Palm oil is an edible plant oil derived from the pulp of the fruit of the oil palm (Palm Oil 2010). Thus, the idea to use palm oil as the biodiesel feedstock was not suitable any more as it will create shortage in food supply chain.

2.3.3 Biodiesel from Jatropha Curcas

Jatropha oil is vegetable oil produced from the seeds of the Jatropha curcas, a plant that can grow in marginal lands and common lands. When jatropha seeds are crushed, the resulting jatropha oil can be processed to produce a high-quality biodiesel that can be used in a standard diesel car, while the residue (press cake) can also be processed and used as biomass feedstock to power electricity plants or used as fertilizer (it contains nitrogen, phosphorous and potassium) (Oil, 2010)

Figure 2.1: Jatropha Curcas

The plant may yield more than four times as much fuel per hectare as soybean, and more than ten times that of maize (corn). A hectare of jatropha has been claimed to produce 1,892 liters of fuel. Goldman Sachs recently cited Jatropha curcas as one of the best candidates for future biodiesel production (Oil, 2010) Jatropha is one of the vegetable oil. However, it is categorized as non-edible vegetable because the seeds and leaves are poisonous. Thus, it will not effecting the food supply chain.

2.4 Transesterification of vegetable oils

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

Alcohols are primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms. The alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. However methanol is preferable because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Supercritical methanol for biodiesel production was first studied by Saka and his co-workers. This has the advantage of allowing a greater range and water content of feedstock (particularly used cooking oil), the product does not need to be washed to remove catalyst, and is easier to design as a continuous process. In this research, the vegetable oil used is jatropha oil.

The factor lead to this selection is because it is non-edible oil. The leaves and nuts are poisonous. Many research and bio-fuel production widely used palm oil as the feedstock. As mention earlier, Jatropha oil is an alternative way to prevent the shortage in the food supply chain.

Biodiesel, define as fatty acid methyl ester, (FAME), is derived from triglycerides by transesterification of alcohols. The Transesterification reaction proceeds without using primary or secondary monohydric alcohol having 1-8 carbon atoms as follow (Eun-Seok Song, 2007)

$$\text{Triglycerides} + \text{Monohydric alcohol} \leftrightarrow \text{Fatty Acid Methyl Ester} +. \text{Glycerin} \quad (2.1)$$

Excess methanol required in order to shift the equilibrium reaction to the right hence increase the formation of methyl ester. 1 mol of triglycerides reacts with 3 moles of alcohol to produce 3 moles fatty acid methyl ester and 1 mol of glycerin.

$$1\ \text{TG} + 3\ \text{MeOH} \longleftrightarrow 3\ \text{FAME} + 1\ \text{GL} \quad (2.2)$$

Biodiesel is made from renewable sources and has become attractive because of its environmental benefit (Hengwen Han, 2005). Biodiesel comes from vegetable or animal fat, making it biodegradable and nontoxic. It has been proven that diesel fuels have viscosities close to those of diesel fuel and has high cetane numbers and flash points (Kalam MA, 2002). It is an alternative for fossil fuels, thus biodiesel becoming an area of high concern.

2.4.1 Catalytic transesterification

The catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerol. Complete settling can take as long as 20 h. Washing the ester is a two-step process, which is carried out with extreme care. A water wash solution at the rate of 28% by volume of oil and g of tannic acid/liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear (Demirbas.A 2005).

2.4.2 Non-catalytic Supercritical Methanol Transesterification

The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol and butanol, has proved to be the most promising process. Table 2.2 shows critical temperatures and critical pressures of various alcohols. A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids.

Table 2.2: Critical temperature and critical pressures of various alcohol.

Alcohol	Critical Temperature, (K)	Critical pressure, (MPa)
Methanol	512.2	8.1
Ethanol	516.2	6.4
1-propanol	537.2	5.1
1-butanol	560.2	4.9

A reaction mechanism of vegetable oil in SCM was proposed based on the mechanism developed by Krammer and Vogel for the hydrolysis of esters in sub/supercritical water (Komers.K et al.). The basic idea of supercritical treatment is a relationship between pressure and temperature upon thermophysical properties of the solvent such as dielectric constant, viscosity, specific weight, and polarity (Krammer et al.) The most important variables affecting the methyl ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature. Viscosities of the methyl esters from the vegetable oils were slightly higher than that of no. 2 diesel fuel.

The variables affecting the ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil, reaction temperature, reaction time, water content and catalyst. It was observed that increasing the reaction temperature, especially to supercritical temperatures, had a favorable influence on ester conversion (Demirbas.A 2002). In the supercritical alcohol transesterification method, the yield of conversion raises 50–95% for the first 10 min. Transesterification reaction of rapeseed oil in SCM has been investigated without using any catalyst. In addition, it was found that this new SCM process requires the shorter reaction time and simpler purification procedure because of the unused catalyst (Demirbas.A 2002).

However, the reaction of methanol and vegetable oil alone are not practicable in the industry. This is because the processes require temperature of 350-400 ^{0}C and pressures of 45-65 MPa, which are not viable in practice in industry. Besides, that such high temperatures and pressure lead to high production cost and energy consumption. To overcome this problem, additional of co-solvent into this reaction is proposed. A co-solvent was added to the reaction mixture in order to decrease the operating pressure, temperature and molar ratio of alcohol to vegetable oil. With carbon dioxide as co-solvent in the reaction system, there was a significant decrease in the severity of the condition required for supercritical reaction, which make the production of biodiesel using supercritical methanol viable as an industrial process (Hengwen Han, 2005).

The solubility of vegetable oil in methanol increases at a rate of 2 ± 3 % (w/w) per 10°C as the reaction temperature is increased (Ma F, 1998). It is thus of great interest from a practical point of view to investigate the use of the co-solvent, which can increase the mutual solubility of methanol and vegetable oil at low reaction temperature. The variables affecting the methyl ester yield during the transesterification reaction are temperature, pressure, molar ratio of methanol and vegetables oil and molar ratio of methanol and co-solvent.

2.5 Reaction mechanism of transesterification

The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol (Eqs. 8–11). The formation of alkyl esters from monoglycerides is believed as a step which determines the reaction rate, since monoglycerides are the most stable intermediate compound (Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70:1–15).

$$\text{Fatty acid } (R_1COOH) + \text{Alcohol } (ROH) \longleftrightarrow \text{Ester } (R_1COOR) + \text{Water } (H_2O) \quad (2.3)$$

$$\text{Triglycerides} + ROH \longleftrightarrow \text{Diglyceride} + RCOOR_1 \quad (2.4)$$

$$\text{Diglyceride} + \text{ROH} \longleftrightarrow \text{Monoglyceride} + \text{RCOOR}_2 \qquad (2.5)$$

$$\text{Monoglyceride} + \text{ROH} \longleftrightarrow \text{Glycerol} + \text{RCOOR}_3 \qquad (2.6)$$

When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis.

2.5.1 Non-catalytic Supercritical Reaction Mechanism

A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. It is evident that at subcritical state of alcohol, reaction rate is very low and gradually increases as either pressure or temperature rises. It was observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on the yield of ester conversion (Demirbas A.2005). In the supercritical alcohol transesterification method, the yield of conversion raises 50–95% for the first 10 min (Demirbas. A 2005).

Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation consumes catalyst and reduces catalyst effectiveness. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water affected positively the formation of methyl esters in supercritical methanol method. Figure 2.2 shows the plots for yields of methyl esters as a function of water content in transesterification of triglycerides. Figure 2.3 shows the plots for yields of methyl esters as a function of free fatty acid content in biodiesel production.

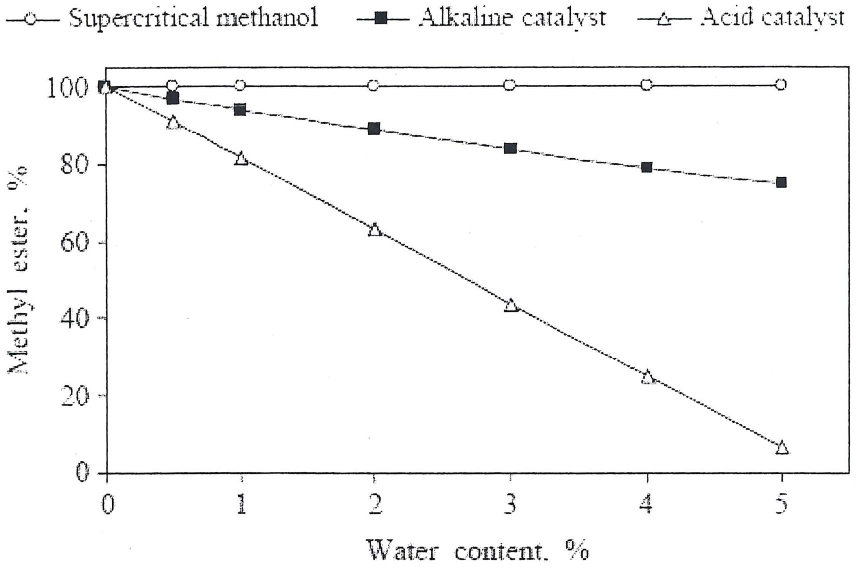


Figure 2.2: Plots of yields of methyl esters as a function of water content in transesterification of triglycerides.

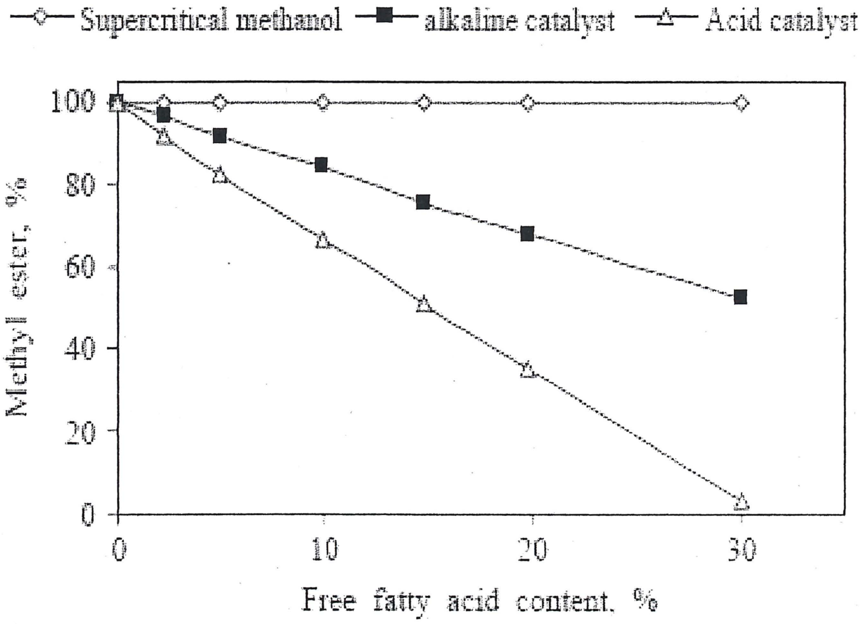


Figure 2.3: Plots for yields of methyl esters as a function of free fatty acid content

2.6 Supercritical methanol and CO_2 transesterification

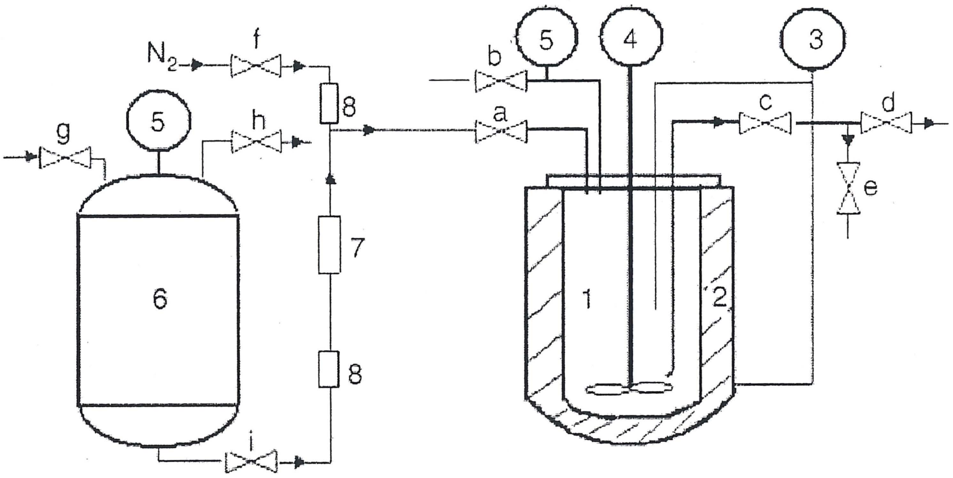


Figure 2.4 : Supercritical methanol and co-solvent transesterification system

Supercritical CO_2 is a good solvent for small and moderate organic molecule and it is a low-cost and facile material (Lang X, 2001) .Therefore, CO_2 is used as the co-solvent in this study and have made a fundamental study of the transesterification of jatropha oil in methanol under supercritical conditions in the presence of CO_2 to investigate the possibility of converting soybean oil to methyl esters as biodiesel fuels.

It is believed that addition of an appropriate co-solvent can decrease the critical point of methanol, and allow the supercritical reaction to be carried out under milder condition (Pak SC, 1972). That is the purpose of additional of co-solvent in the process. The co-solvent can reduce the supercritical condition due to the dipole moment and dielectric constant value. Usually, the co-solvent has lower value of dipole moment and dielectric constant. Before reach the supercritical state, the oil and methanol are in binary phase. It requires high energy to convert to single phase.

Propane and hexane are excellent solvent for vegetable oil to be use in the study. It showed that the use of co-solvent is feasible. Thus, in this study, CO_2 is used as the co-solvent. CO_2 is added to the reaction system in order to increase the mutual solubility between methanol and oil under supercritical conditions (W. Cao et al.)

2.6.1 Properties of Methanol

Also called Methyl Alcohol, it is the simplest of a long series of organic compounds called alcohols; its molecular formula is CH_3OH. The modern method of preparing methanol is based on the direct combination of carbon monoxide gas and hydrogen in the presence of a catalyst at elevated temperatures and pressures. Most methanols is produced from the methane component of natural gas. (CEC, 2010)

Pure methanol is an important material in chemical synthesis. Its derivatives are used in great quantities for building up a vast number of compounds, among them many important synthetic dyestuffs, resins, drugs, and perfumes. Large quantities are converted to dimethylaniline for dyestuffs and to formaldehyde for synthetic resins. It is also used in automotive antifreezes, in rocket fuels, and as a general solvent. Methanol is also a high-octane, clean-burning fuel that is a potentially important substitute for gasoline in automotive vehicles (CEC, 2010)

Methanol is a colorless liquid, completely miscible with water and organic solvents and is very hygroscopic. It boils at 64.96° C (148.93° F) and solidifies at -93.9° C (-137° F). It forms explosive mixtures with air and burns with a nonluminous flame. It is a violent poison; drinking mixtures containing methanol has caused many cases of blindness or death. Methanol has a settled odor. Methanol is a potent nerve poison. Key physical properties are in Table 2.3.

Table 2.3: Physical Properties of Methanol

Properties	**Value**
Melting Point	-97.7 ^{0}C
Boiling Point	65 °C
Relative Density	0.79
Molecular weight:	32.042 kg/kmol
Heat of Formation	-201.3 MJ/kmol
Gibbs Free Energy	-162.62 MJ/kmol
Boiling point	64.6 °C(at atmospheric pressure)
Freezing point	-97.7 °C
Density	791 kg/m^3 at 20 °C

Source: Certiner Engineering Corporation,CEC 2010

Table 2.4: Critical Properties of Methanol

Properties	**Value**
Critical temperature	512.6 K
Critical pressure	81 bar abs
Critical volume	0.118 m^3/kmol

Source: Certiner Engineering Corporation,CEC 2010

It is toxic: drinking 10 ml will cause blindness, and as little as 100 ml will cause death. It is the simplest alcohol, and is a light, volatile, colorless, flammable, liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol (drinking alcohol) (Lang X, 2001). At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. It is also used for producing biodiesel via transesterification reaction. The critical point of methanol occurs at 239.4^{0}C and the dielectric constant is 32.6.

2.6.2 Properties of CO_2

At standard temperature and pressure, the density of carbon dioxide is around 1.98 kg/m^3, about 1.5 times that of air. The carbon dioxide molecule (O=C=O) contains two double bonds and has a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable, but will support the combustion of metals such as magnesium (Lenntech, 1999)

At −78.51°C, carbon dioxide changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition. Solid carbon dioxide is normally called "dry ice", a generic trademark. It was first observed in 1825 by the French chemist Charles Thilorier. Dry ice is commonly used as a cooling agent, and it is relatively inexpensive. A convenient property for this purpose is that solid carbon dioxide sublimes directly into the gas phase leaving no liquid. It can often be found in grocery stores and laboratories, and it is also used in the shipping industry. The largest non-cooling use for dry ice is blast cleaning (Lenntech, 1999)

Table 2.5: Physical Properties of CO_2

Properties	**Value**
Melting Point	-78 ^{0}C
Boiling Point	-57 ^{o}C
Molecular weight:	44.01 kg/kmol
Density	0.77 kg/m^3 at 20 °C
Viscosity	0.07 cp at -78 ^{o}C

Source: Lenntech, 1999

Liquid carbon dioxide forms only at pressures above 5.1 atm; the triple point of carbon dioxide is about 518 kPa at −56.6 °C. The critical point is 7.38 MPa at 31.1 °C and the dielectric constant is 1.00.

Table 2.6: Critical properties of CO_2

Critical properties	**Value**
Critical temperature	31.1°C
Critical pressure	7.4 MPa
Critical density	468 kg/m^3

Source: Lenntech,1999

2.7 Dielectric Constant

A dielectric material is any material that supports charge without conducting it to a significant degree. Dielectric materials are used in many applications, from simple electrical insulation to sensors and circuit components. A dielectric supports charge by acquiring a polarisation in an electric field. There are three main polarisation mechanisms that can occur within a dielectric material: electronic polarisation, ionic polarisation (sometimes referred to as atomic polarisation) and orientational polarization ((DoITPoMS, 2008).

The definition of the dielectric constant relates to the permittivity of the material. Permittivity is a quantity that describes the effect of a material on an electric field: the higher the permittivity, the more the material tends to reduce any field set up in it. Since the dielectric material reduces the field by becoming polarised, an entirely equivalent definition is that the permittivity expresses the ability of a material to polarise in response to an applied field. The dielectric constant (sometimes called the 'relative permittivity') is the ratio of the permittivity of the dielectric to the permittivity of a vacuum, so the greater the polarisation developed by a material in an applied field of given strength, the greater the dielectric constant will be ((DoITPoMS, 2008).

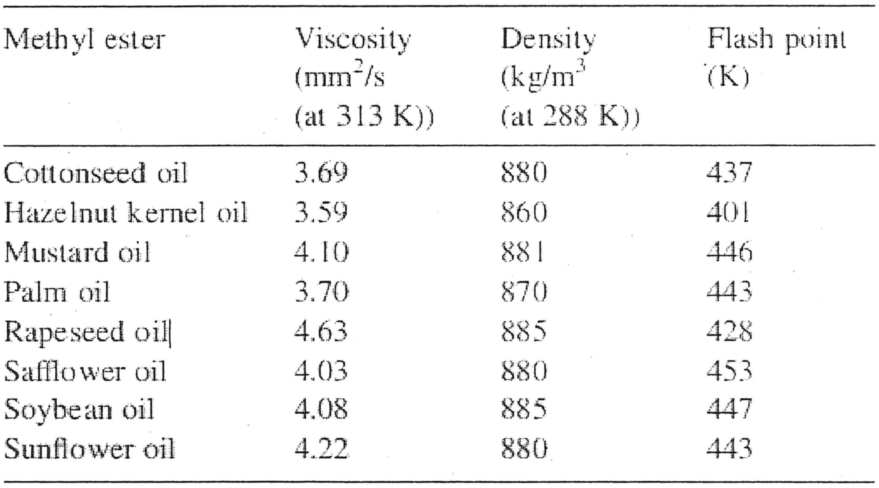
The more available polarisation mechanisms a material possesses, the larger its dielectric constant will be. For example, materials with permanent dipoles have larger dielectric constants than similar, non-polar materials. The more easily the various polarisation mechanisms can act, the larger the dielectric constant will be. For polar structures, the magnitude of the dipole also affects the magnitude of polarisation achievable, and hence the dielectric constant. A polar gas tends to have smaller dipoles, and its low density also means there is less to polarise, therefore polar gases have lower dielectric constants than polar solids or liquids. The density argument also applies for non-polar gases when compared with non-polar solids or liquids ((DoITPoMS, 2008).

2.8 Properties of Biodiesel

Vegetable oils can be used as fuel for combustion engines, but its viscosity is much higher than usual diesel fuel and requires modifications of the engines. The major problem associated with the use of pure vegetable oils as fuels, for diesel engines are caused by high fuel viscosity in compression ignition. Therefore, vegetable oils are converted into their methyl esters by transesterification. Viscosity is a measure of the internal friction or resistance of an oil to flow. As the temperature of oil is increased, its viscosity decreases and it is therefore able to flow more readily (Demirbas.A 2005)

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has viscosity close to diesel fuels.

High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. A novel process of biodiesel fuel production has been developed by a non-catalytic supercritical methanol method (Demirbas.A 2005)



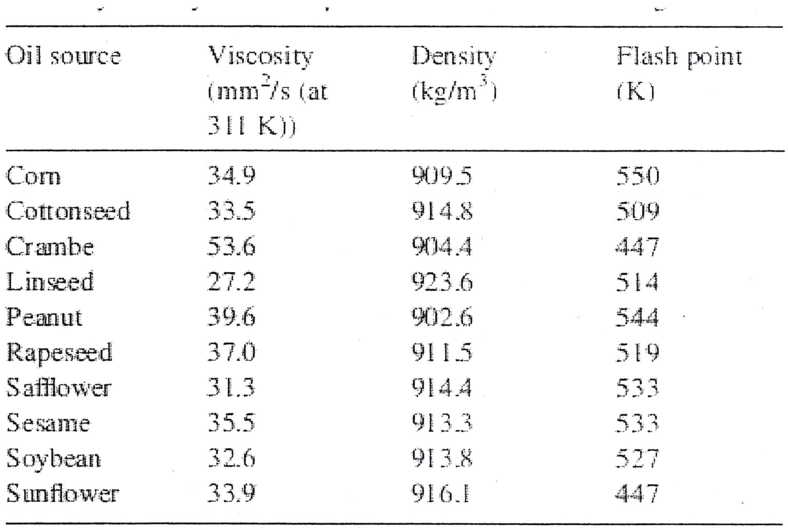
Methyl ester	Viscosity (mm^2/s (at 313 K))	Density (kg/m^3 (at 288 K))	Flash point (K)
Cottonseed oil	3.69	880	437
Hazelnut kernel oil	3.59	860	401
Mustard oil	4.10	881	446
Palm oil	3.70	870	443
Rapeseed oil	4.63	885	428
Safflower oil	4.03	880	453
Soybean oil	4.08	885	447
Sunflower oil	4.22	880	443

Figure 2.5: Viscosity, density and flash point measurements of eight oil methyl esters

Source: Demirbas,2005

Viscosity, density and flash point measurements of eight oil methyl esters are given in Figure 2.5. Compared to no. 2 diesel fuel, all of the vegetable oils were much more viscous. Viscosity, density and flash point measurements of ten vegetable oils given by Goering et al. are shown in Figure 2.5(Goering et al.1982). The density values of vegetable oils are between 902.6 and 923.6 kg/m3 while those of vegetable oil methyl esters are between 860 and 885 kg/m3 (Figure 2.6). The density values of vegetable oil methyl esters considerably decreases via transesterification process. The viscosity values of vegetable oils are between 27.2 and 53.6 mm2/s whereas those of vegetable oil methyl esters are between 3.59 and 4.63 mm2/s. The viscosity values of vegetable oil methyl esters highly decreases after transesterification process. Compared to no. 2 diesel, all of the vegetable oil methyl esters were slightly viscous. The flash point values of vegetable oil methyl esters are highly lower than those of vegetable oils (Figure 2.5 and 2.6).

Density is another important property of biodiesel. It is the weight of a unit volume of fluid. Specific gravity is the ratio of the density of a liquid to the density of water. Specific gravity of biodiesel fuels ranges between 0.87 and 0.89 kg/m^3 (Table 2.5). Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel (Demirbas.A 2005)



Oil source	Viscosity (mm^2/s (at 311 K))	Density (kg/m^3)	Flash point (K)
Corn	34.9	909.5	550
Cottonseed	33.5	914.8	509
Crambe	53.6	904.4	447
Linseed	27.2	923.6	514
Peanut	39.6	902.6	544
Rapeseed	37.0	911.5	519
Safflower	31.3	914.4	533
Sesame	35.5	913.3	533
Soybean	32.6	913.8	527
Sunflower	33.9	916.1	447

Figure 2.6: Viscosity, density and flash point measurements of 10 vegetable oils

Source: Demirbas 2005

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, the focus is on the research methodology and experimental procedures. The research methodology covers selecting raw material, design of experiment, experiment procedures, and sample analysis. There are two main equipments used in this research, which is supercritical reactor unit made of Switzerland and rotary evaporator from Fischer. The critical condition and availability is the guideline to select the suitable raw material. The process seems very simple but it required minimum a day to obtain one pure sample product. According to design of experiment, there are 27 experiments are carried out.

3.2 Supercritical Reactor

The supercritical reactor is an equipment that allows reaction to take place at high temperature and pressure up to 400^0C and 200 bar, respectively. The dimension of this reactor is 1.38 meter height, 0.7 m width, 0.705 m depth without agitator drive with weigh approximately 100 kg. The maximum capacity of the reactor vessel is 2.0 liter. The maximum load of reactor is 150 kg and the hydraulic pump will protect the overload. The hydraulic system is filled with oil and vented. The vessel of the reactor can be lift, lower and tilt.

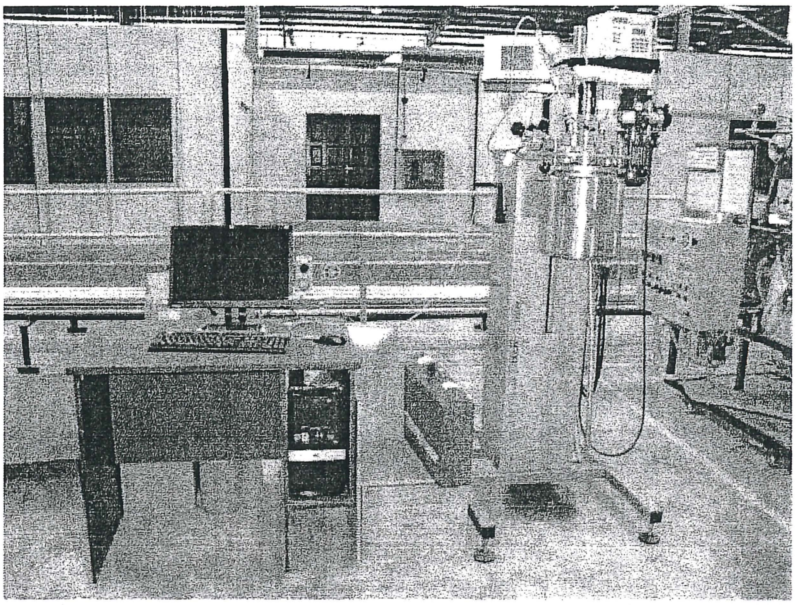


Figure 3.1: Supercritical reactor Buchi Asusler Limbo 350 la, Switzerland

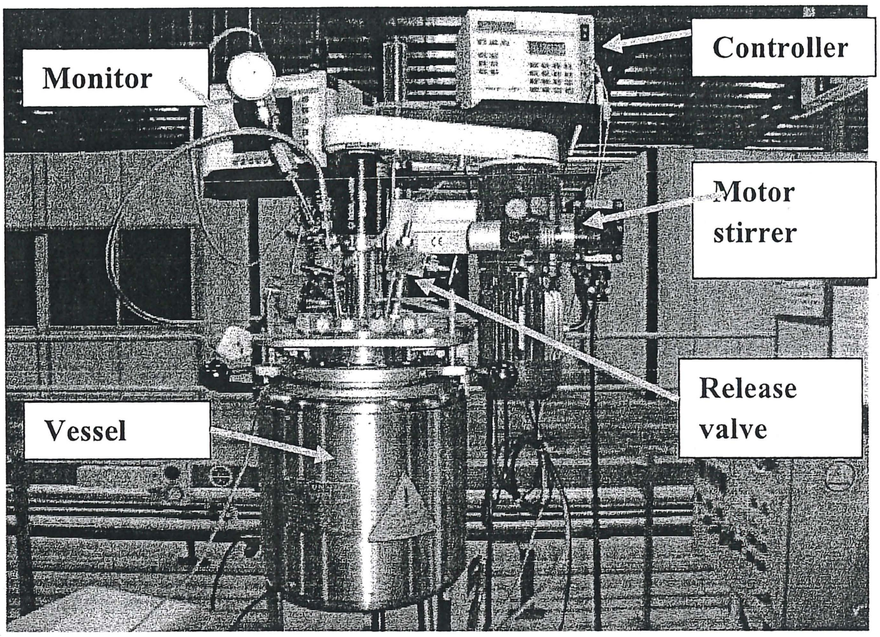


Figure 3.2: Main component of supercritical reactor

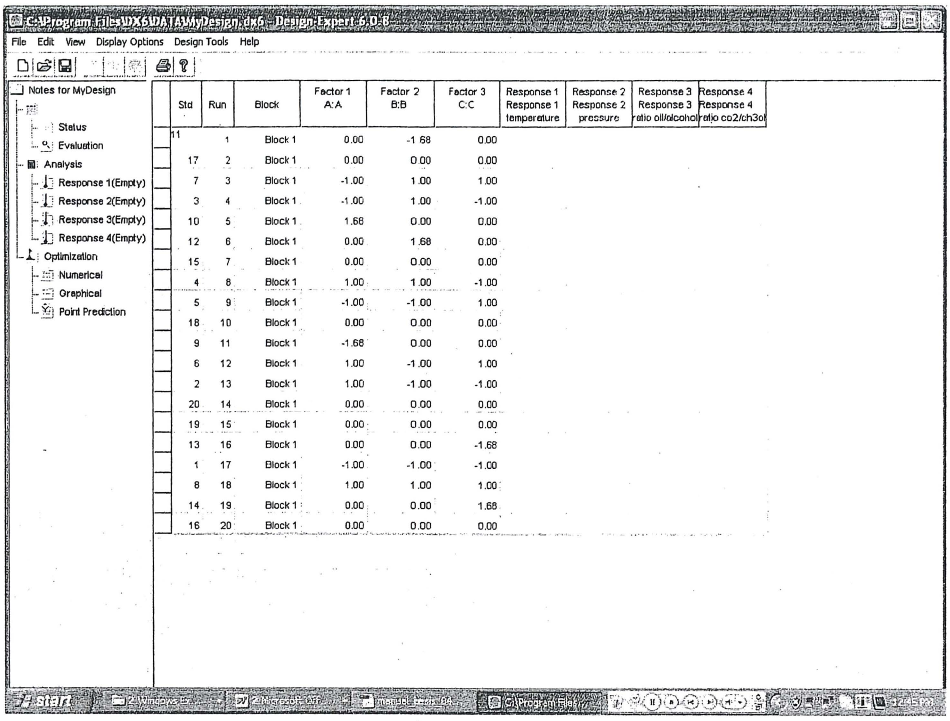
There are five main components of supercritical reactor as shown in Figure 3.2. The function of controller is to set up the desired temperature, pressure and duration of reaction. The temperature is set up based on reaction temperature, T_R. The monitor allows monitoring the temperature, pressure and stirring speed at real time and equipped with alarm to prevent overheating. Motor stirrer used to stir the mixture inside the vessel at different speed and can stir up to 4000 rpm. Release valve used to release undesired gases to reduce the pressure inside vessel. In this study, after the reaction completed, CO_2 is removed from the system via release valve. As mention earlier, the vessel (reactor) capacity is 2 L. However, the maximum capacity of mixture feed in is 1.5 L in order to give some space for mixture to react.

3.3 Materials Selection

In order to select the appropriate material, the critical temperature of solvent and co-solvent must be identified. The raw materials used in this study are refined jatropha oil purchased from Otazh Biotech Sdn .Bhd, high grade methanol (solvent) purchased from Dinshem Technologies Sdn. Bhd and Carbon dioxide,CO_2 (co-solvent) purchased from MOX Sdn.Bhd

3.4 Design of Experiment

Design-Expert 6.0.8 is used to design the pattern of experiment depending on the parameters selected. This software can be used to design 2 to 15 factors where each factor is varied over 2 levels. It is useful for estimating main effects and interactions. Fractional factorial can be used for screening many factors to find the significant few. In this work, the number of factorial is 3 as it have 3 parameters.



Std	Run	Block	Factor 1 A:A	Factor 2 B:B	Factor 3 C:C	Response 1 Response 1 temperature	Response 2 Response 2 pressure	Response 3 Response 3 ratio oil/alcohol	Response 4 Response 4 ratio co2/ch3o
11	1	Block 1	0.00	-1.68	0.00				
17	2	Block 1	0.00	0.00	0.00				
7	3	Block 1	-1.00	1.00	1.00				
3	4	Block 1	-1.00	1.00	-1.00				
10	5	Block 1	1.68	0.00	0.00				
12	6	Block 1	0.00	1.68	0.00				
15	7	Block 1	0.00	0.00	0.00				
4	8	Block 1	1.00	1.00	-1.00				
5	9	Block 1	-1.00	-1.00	1.00				
18	10	Block 1	0.00	0.00	0.00				
9	11	Block 1	-1.68	0.00	0.00				
6	12	Block 1	1.00	-1.00	1.00				
2	13	Block 1	1.00	-1.00	-1.00				
20	14	Block 1	0.00	0.00	0.00				
19	15	Block 1	0.00	0.00	0.00				
13	16	Block 1	0.00	0.00	-1.68				
1	17	Block 1	-1.00	-1.00	-1.00				
8	18	Block 1	1.00	1.00	1.00				
14	19	Block 1	0.00	0.00	1.68				
16	20	Block 1	0.00	0.00	0.00				

Figure 3.3: Design of experimental

3.5 Experimental Procedures

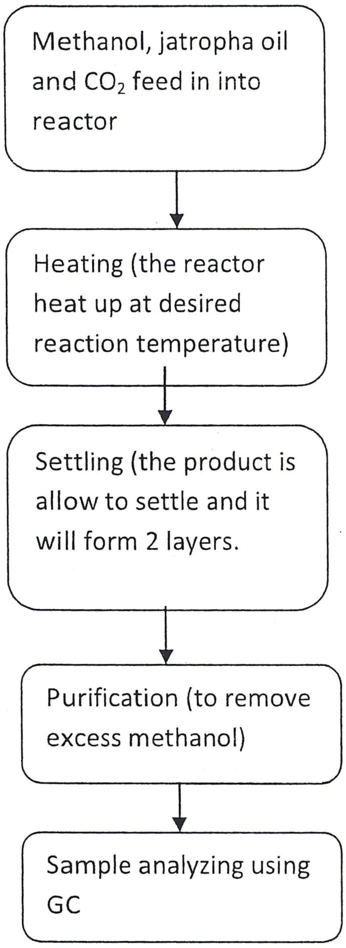


Figure 3.4: Flowchart of experimental procedures

3.5.1 Feed in

Jatropha oil and methanol were loaded into the reactor with prescribed mole ratio. The CO_2 is supply at appropriate volume using 10 mm tubing controlled by pressure regulator before the reactor is heat up. After all the materials loaded into reactor, the 12 screws need to be tightened and make sure all the valve are closed.

3.5.2 Heating

The reactor is heated up at desired reaction temperature. Longer time is required to achieve higher reaction temperature. For example, the duration needed to achieve reaction temperature of 160°C is 45 minutes. However, at reaction temperature of 230 and 300°C the required time is about 115 minutes and 150 minutes, respectively. The reaction time is fixed at 5 minutes. After the reaction temperature achieved and constant about 5 minutes, the reactor is started to cool down until reach room temperature before the product withdrawn.

3.5.3 Settling

The product sample withdrawn is allowed to settle about 20 to 24 hours. The two layers will form. The upper layer is known as methyl ester is the main product and the lower layer is glycerol as by product. However, the glycerol is removed from the layer for further purification.

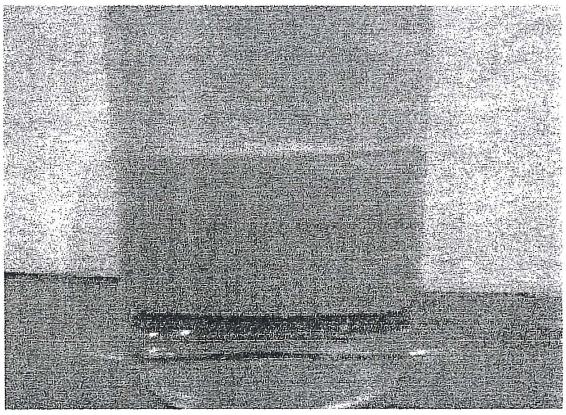


Figure 3.5: Product with two layers formed

3.5.4 Purification

For purification process, the product samples undergo the distillation process where rotary evaporator is used to remove excess methanol. The temperature is fixed at 70°C in order to vaporize excess methanol as it is the boiling point of methanol. The purpose of removing methanol from the product sample is to prevent methanol from reacts with hexane. Hexane HPLC grade is used as the solvent for sample analysis.

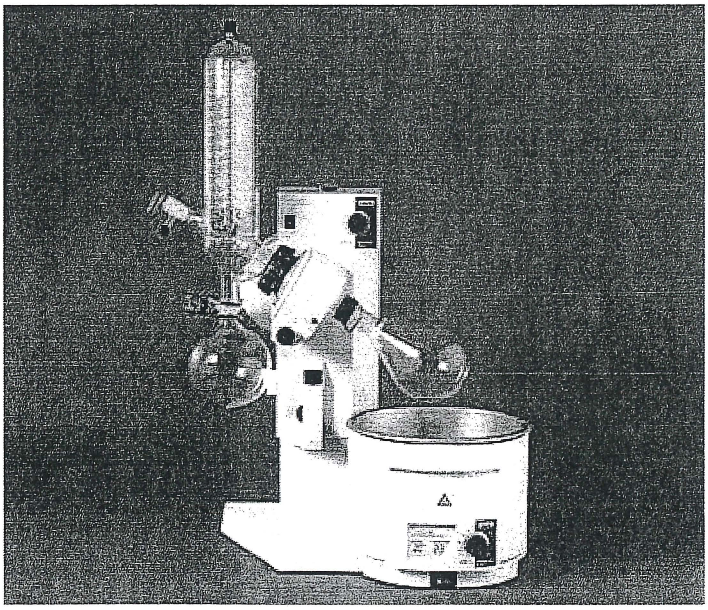


Figure 3.6: Rotary evaporator

3.5.5 Method of Analyzing

In order to prepare sample for analysis, the product sample is weighted at 115 mg and mixed with 5 ml of Hexane HPLC grade. The mixture is shaking vigorously. 1.5 ml of mixture placed into a vial and proceeds for analysis using gas chromatography- mass spectrometer (GC-MS). The process required 24 hours in order to obtain accurate results. The same procedure was repeated using different condition.

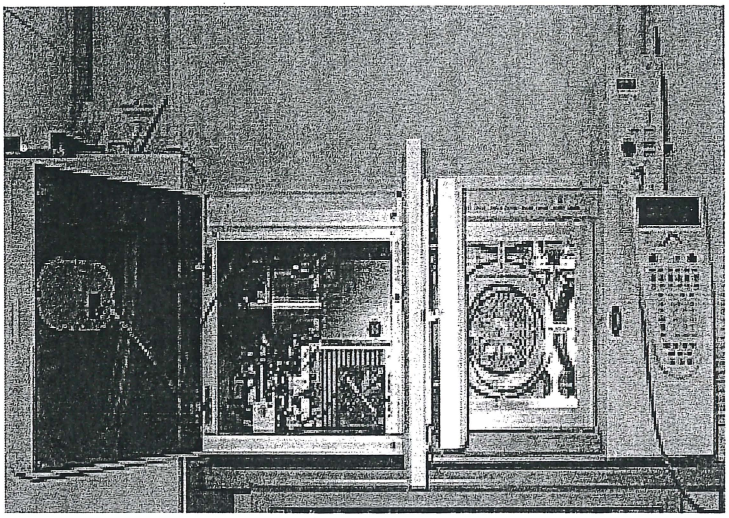
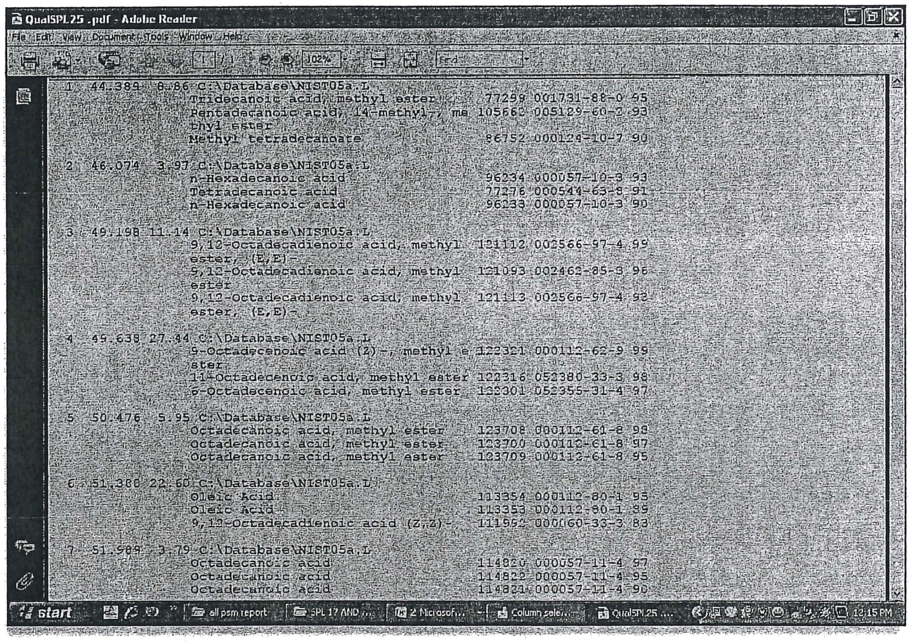


Figure 3.7: The insides of the GC-MS, with the column of the gas chromatograph in the oven on the right.

3.6 Sample Analysis

The composition and yield of methyl ester in the product samples were analyzed using gas chromatography equipped with mass spectrometer (GC-MS). Hexane was used as solvent while helium gas was used as the carrier gas. The identification of the peaks of the various methyl esters was estimated by comparing the retention time of each compound in the sample with the standard compound. The yield of Jatropha Oil Methyl Ester was then calculated using the ratio of the peak area of the sample to the standard. One of the characteristic of fatty acid methyl ester (FAME) is to consist of C_{18}.

The fatty acid names are Octadecenoic acid (Stearic acid), *cis*-9-Octadecenoic acid (Oleic acid), *trans*-9- Octadecenoic acid (Elaidic acid), all *cis*-9,12-Octadecadienoic acid (Linoleic acid), all *trans*-9,12- Octadecadienoic acid(Linolelaidic acid) and all *cis*-9,12,15- Octadecatrienoic acid (alpha Linolenic acid).



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1  44.389  8.86 C:\Database\NIST05a.L
                Tridecanoic acid, methyl ester       77299 001731-88-0 95
                Pentadecanoic acid, 14-methyl-, me 105662 005129-60-2 93
                thyl ester
                Methyl tetradecanoate                86752 000124-10-7 90

2  46.074  3.97 C:\Database\NIST05a.L
                n-Hexadecanoic acid                  96234 000057-10-3 93
                Tetradecanoic acid                   77276 000544-63-8 91
                n-Hexadecanoic acid                  96233 000057-10-3 90

3  49.198 11.14 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
                ester, (E,E)-
                9,12-Octadecadienoic acid, methyl  121093 002462-85-3 96
                ester
                9,12-Octadecadienoic acid, methyl  121113 002566-97-4 93
                ester, (E,E)-

4  49.638 27.44 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                ster
                11-Octadecenoic acid, methyl ester 122316 052380-33-3 98
                6-Octadecenoic acid, methyl ester  122301 052355-31-4 97

5  50.476  5.95 C:\Database\NIST05a.L
                Octadecanoic acid, methyl ester    123708 000112-61-8 98
                Octadecanoic acid, methyl ester    123700 000112-61-8 97
                Octadecanoic acid, methyl ester    123709 000112-61-8 95

6  51.380 22.60 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 95
                Oleic Acid                         113353 000112-80-1 89
                9,12-Octadecadienoic acid (Z,Z)-   111952 000060-33-3 83

7  51.989  3.79 C:\Database\NIST05a.L
                Octadecanoic acid                  114820 000057-11-4 97
                Octadecanoic acid                  114822 000057-11-4 95
                Octadecanoic acid                  114821 000057-11-4 90
```

Figure 3.8: Result analysis

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

It can be assumed that the transesterification of jatropha oil in supercritical methanol proceeds by the same reaction mechanism as that for transesterification with liquid methanol. It is believed that CO_2 has no effect on the reaction mechanism. Transesterification is an equilibrium reaction. In the system, an excess of methanol was used in order to shift the equilibrium to the right and produce more methyl esters as product (W. Cao et al).

Reaction of supercritical methanol with jatropha oils were carried out in a batch-type reaction vessel. In all of the experiments, the reaction time was kept constant. Therefore, the reaction temperature and pressure inside the reaction vessel vary with reaction condition. Critical points for the binary system are determined by the content of CO_2 in the binary system. It was found that the critical points of the binary system were achieved at temperatures, which decrease with increasing molar ratio of CO_2 to methanol (W. Cao et al).

The graph and data obtained from analyzed sample product used to determine the amount methyl ester contained as shown at Figure 4.1. To determine the effect of temperature on methyl esters formation, transesterification reactions of jatropha oil were carried out with a fixed reaction time of 5 minutes at various temperatures ranging from 160 to 300°C. Figure 4.2, 4.3 and 4.4 shows the effect of CO_2 towards reaction pressure and Figure 4.5, 4.6 and 4.7 shows the effect of CO_2 and mole ratio of oil/alcohol towards production of methyl esters.

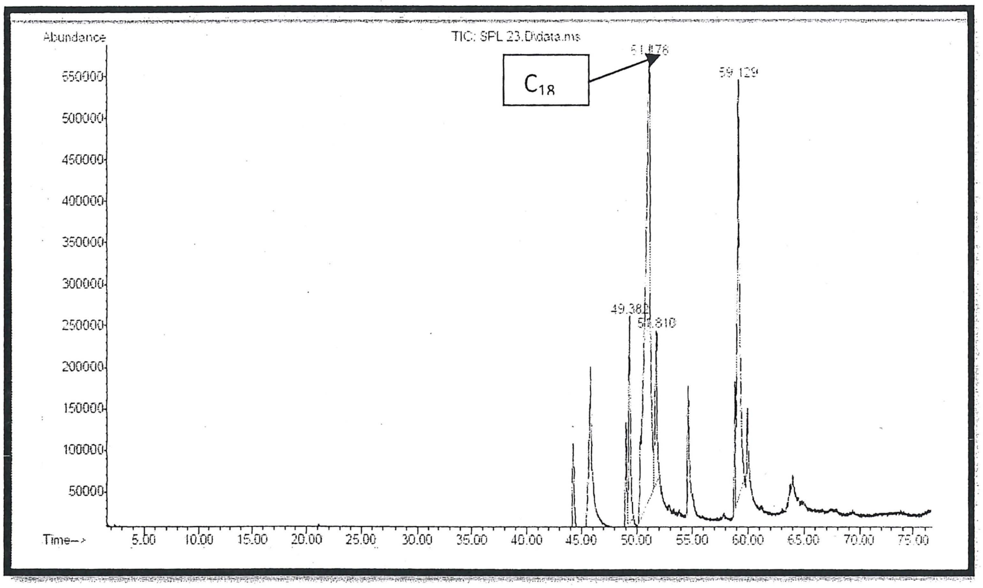

Figure 4.1: GC chromatogram of the transesterification reaction products of jatropha oil

4.2 Effect of CO_2 on Reaction Pressure

Figure 4.2 shows the effect of different volume CO_2 at different reaction temperature on reaction pressure. The volumes of CO_2 used were 0.018 m^3, 0.055 m^3 and 0.092 m^3, respectively. CO_2 will act as co-solvent and reduce the critical point of methanol hence increase the mutual solubility between methanol and jatropha oil under sub/supercritical condition. Results as illustrated in Figure 1 shows that the reaction pressure increases as temperature increased for each volume of CO_2 used.

The lowest reaction pressure was obtained at 160°C (subcritical) reaction temperature with CO_2 volume of 0.092 m^3. At CO_2 volume of 0.018 m^3, there is no significant effect to the pressure when the reaction temperatures increase to 230°C and 300°C. However, at CO_2 volume of 0.055 m^3 0.092 m^3 increasing of reaction temperature beyond 230^0C caused a tremendous increase in reaction pressure. This is because the reaction temperature used already reached the critical point of methanol at 239.4^0C. At this range of reaction temperature, methanol is transform from liquid to gas thus increase the reaction pressure.

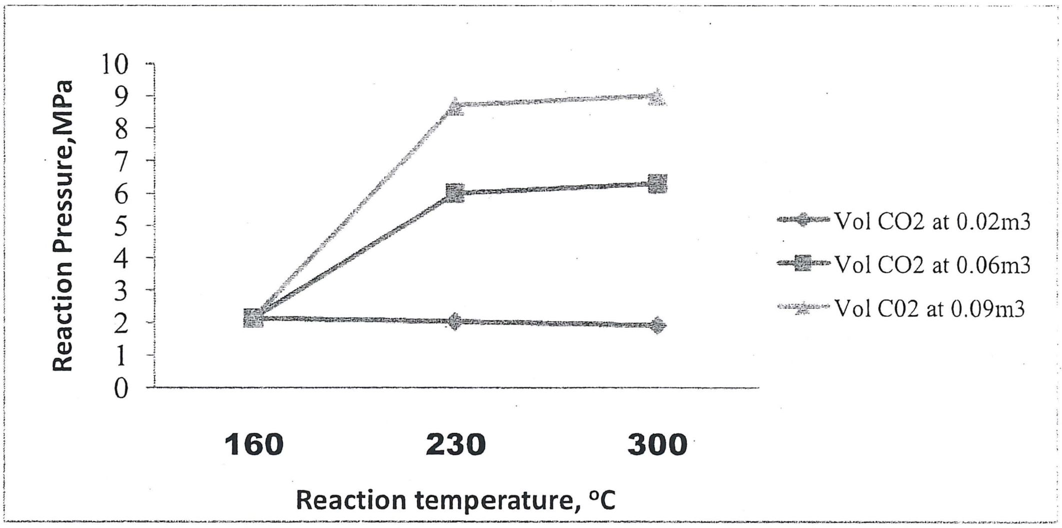

Figure 4.2: Effect of CO_2 on pressure

As mentioned earlier, the significant effect of CO_2 has showed at 160°C. As illustrated in Figure 4.3 the reaction pressure decreased from 2.1 MPa to 1.9 MPa when the CO_2 volume increased from 0.018 m^3 to 0.092 m^3. The addition of co-solvent in transesterification process can reduce the supercritical condition to a subcritical condition due to the lower dipole moment and dielectric constant value. Usually, the co-solvent has lower value of dipole moment and dielectric constant. The higher polarisation mechanisms possesses by a material, the larger its dielectric constant will be. For example, materials with permanent dipoles have larger dielectric constants than the similar non-polar materials. The dielectric constant of CO_2 is 1.00 (non-polar) and for methanol is 32.6 as it is polar material. For materials that possess permanent dipoles, there is a significant variation of the dielectric constant with temperature and pressure. This is due to the effect of heat on polarisation orientation (DoITPoMS, 2008).

However, this does not mean that the dielectric constant will increase continually as temperature is lowered. There are several discontinuities in the dielectric constant as temperature and pressure changes. First of all, the dielectric constant will change suddenly at phase boundaries. This is because the structure changes in a phase change and the dielectric constant is strongly dependent on the structure. Whether the dielectric constant will increase or decrease at a given phase change depends on the exact two phases involved. In order to convert to single phase, the materials must first overcome a certain energy barrier. To overcome the energy barrier of methanol, the CO_2 is added into the system as the dielectric constant of CO_2 is much lower than methanol. An efficient dielectric supports a varying charge with minimal dissipation of energy in the form of heat. Dielectric loss tends to be higher in materials with higher dielectric constants. This is the downside of using these materials in practical applications (DoITPoMS, 2008).

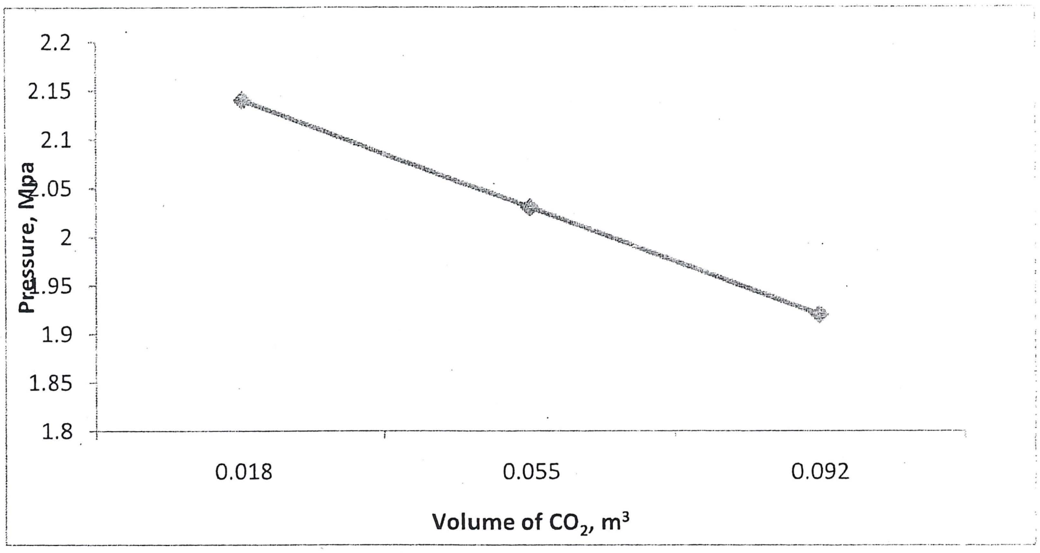

Figure 4.3: Effect of CO_2 on reaction pressure at 160^0C

As mention earlier, the reaction pressure increases as temperature increased for each volume of CO_2 used as shown in Figure 4.4. At reaction temperature of 230^OC, the reaction pressure increases from 15.0MPa to 16.0MPa with increased volume of CO_2 at 7 % increment. At 230^OC and 300^OC, the reaction pressure is high due to the supercritical state of methanol.

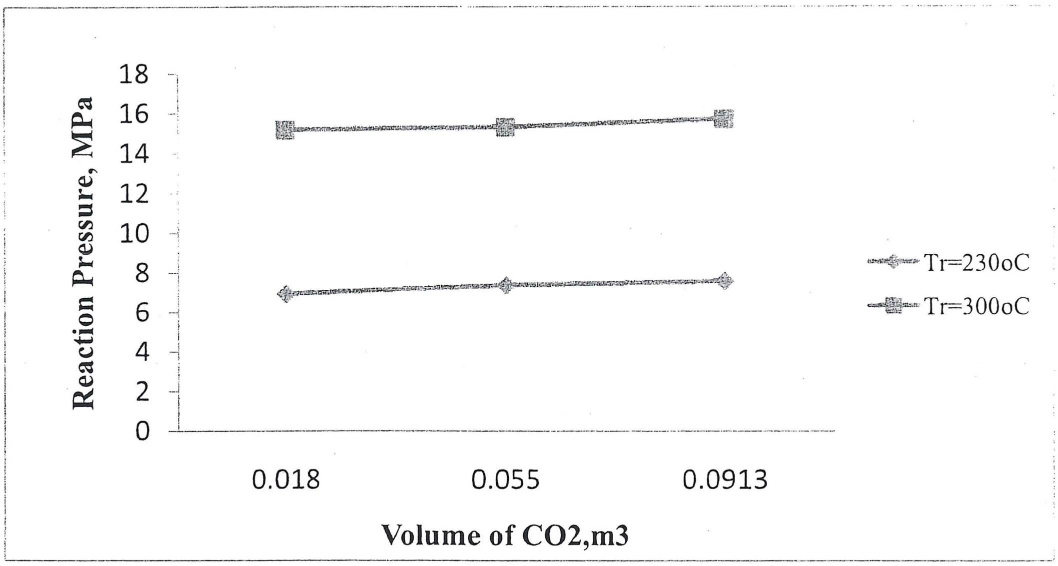

Figure 4.4: Effect of CO_2 on Jatropha Oil Methyl Ester yield at 230°C and 300°C

4.3 Effect of CO_2 on Production of Methyl Ester

Figure 4.5 shows that the effect of CO_2 on JOME yields at reaction temperature of 160°C. The methyl ester was greatly converted (84.3 w/w%) when 0.018 m^3 CO_2 was fed to the system. However, the yield of JOME decreases to 82.2 w/w% and 83 w/w% as the CO_2 volume increase to 0.055 m^3 and 0.092 m^3, respectively. The changes of the JOME yields are relatively small, which is less than 5%. It is revealed that, there is no significant effect towards the yields of methyl ester when CO_2 was employed to the system. However, significant reduction in reaction pressure was obtained.

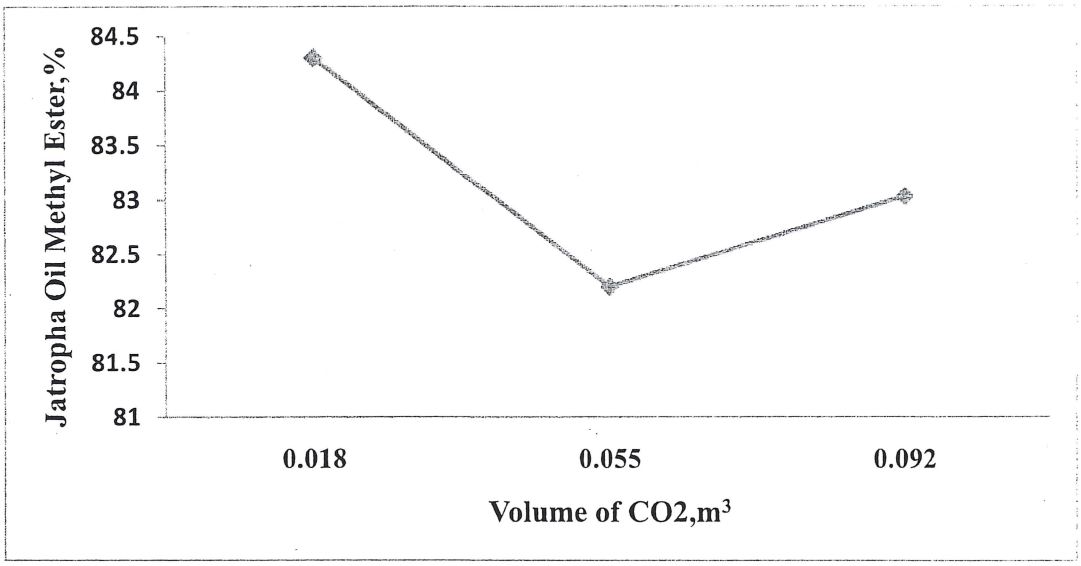

Figure 4.5: Effect of CO_2 on Jatropha Oil Methyl Ester yield at 160^0C

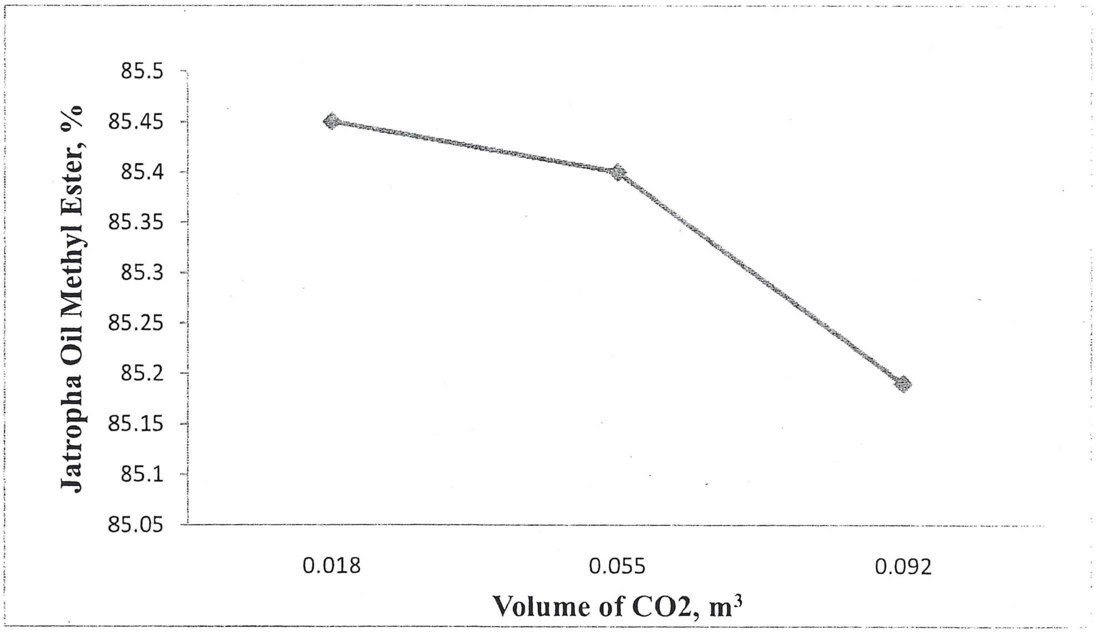

Figure 4.6: Effect of CO2 on Jatropha Oil Methyl Ester at 300°C

It is believed that the optimum ratio of oil/alcohol is in the range of 24 and 42. However, in this research, the highest ratio used is to be 30. Figure 4.5 shows the results of JOME yields at 300°C and mole ratio oil/alcohol at 1:30. The production of JOME is decreasing as the volume CO_2 added rises. Though increasing the volume of CO_2 to methanol decreases the critical point of the system, the optimal temperature for the supercritical reaction does not decrease continuously. Figure 4.6 shows the changes in weight percentage of methyl esters formed with different volume CO_2 and methanol under supercritical conditions as a function of reaction temperature. However, when the ratio reaches a certain point, the optimal temperature remains constant. This indicates that the transesterification reaction has a high energy barrier, and that either a high reaction temperature or the presence of a catalyst is required if the reaction to proceed (W.Cao et.al)From the results obtained, it was found that the optimal temperature is 300°C when the volume of CO_2 is 0.018m^3.

4.4 Effect of Mole Ratio of Oil/Alcohol on Production of Methyl Ester

Higher molar ratios of methanol to oil also result a more result in transesterification reaction, due perhaps to the increased contact area between methanol and triglycerides thus increased the yield production (Saka et al.). However, higher molar ratios of methanol to oil result in increased reaction pressure, which imposes stringent requirement on the reaction vessel. CO_2 is added to the reaction system in order to increase the mutual solubility between methanol and jatropha oil under supercritical conditions. Since CO_2 is a good solvent for vegetable oil, it allows the reaction mixture to form a single phase at a much lower temperature (W. Cao et al.).

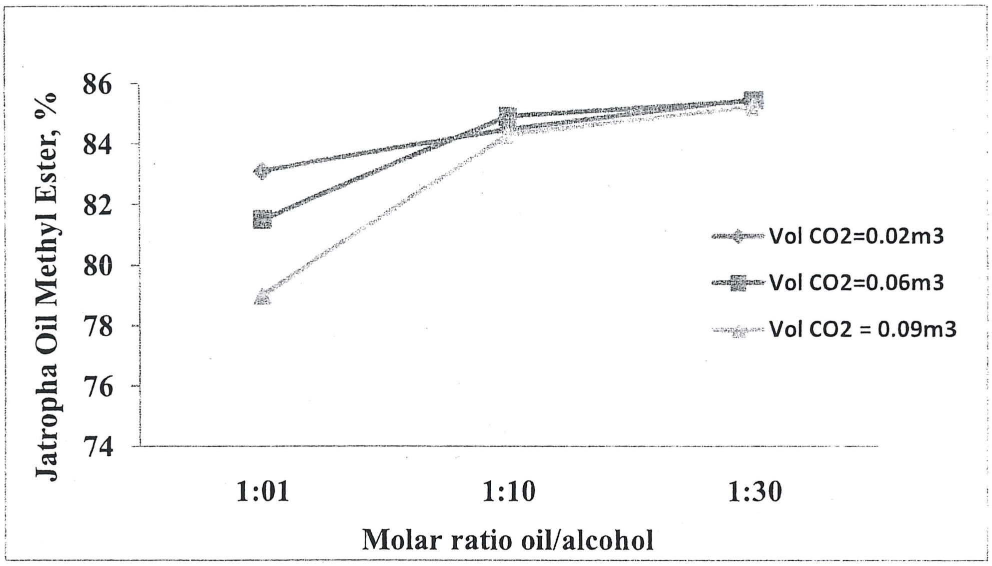

Figure 4.7: Effect of CO_2 at different molar ratio of oil/alcohol

A mixture of methyl esters of vegetable oil, or biodiesel, is very similar to conventional diesel fuel. Its viscosity is only twice that of diesel and its molecular weight is roughly 1/3 that of vegetable oil. The viscosities of the methyl esters obtained from jatropha oil were slightly higher than that of No. 2 diesel. The measured values of the viscosities of the methyl esters were 10 mm^2/s at 40°C.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Non-catalytic supercritical methanol transesterification technology has been shown to be a superior method in biodiesel production in terms of cost and energy consumption. Synthesis of biodiesel from jatropha oil with supercritical methanol is superior to the conventional chemical method. Compared with the conventional method, a less purified process is required.

The purpose of the addition of CO_2 in transesterification of vegetable oils is to reduce the severity of reaction and pressure reaction. It is shown that the subcritical methanol process with CO_2 as a co-solvent is a suitable method in producing biodiesel. Experimental investigations are conducted by using supercritical reactor batch mode with capacity of 2.0 L. As co-solvent, CO_2 is easy to supply into the system and to remove from the reaction after the reaction is completed. The reaction pressure is become lower when CO_2 is added to the system since the critical point of CO_2 is lower than methanol. Result shows that, addition of CO_2 in the reaction system manage to decrease the reaction pressure. The best volume of CO_2 addition obtained from this study was 0.018 m^3 with reaction pressure 15.1 MPa and highest yields is 85.45 w/w% of jatropha oil methyl ester (JOME) at reaction temperature of 300°C. This study shows that, the addition of CO_2 as co-solvent is a promising method to reduce the reaction pressure and acceptable for future studies.

5.2 Recommendations

Here are some recommendations to improve the production of Jatropha Oil Methyl Ester in the future study:

i. The flow of CO_2 added into reactor should be measured using appropriate gas meter flow rate.

ii. The range of reaction temperature should be increased in order to give higher yield.

iii. The result of yield production with and without addition of CO_2 should be compared in order to study the optimal reaction condition.

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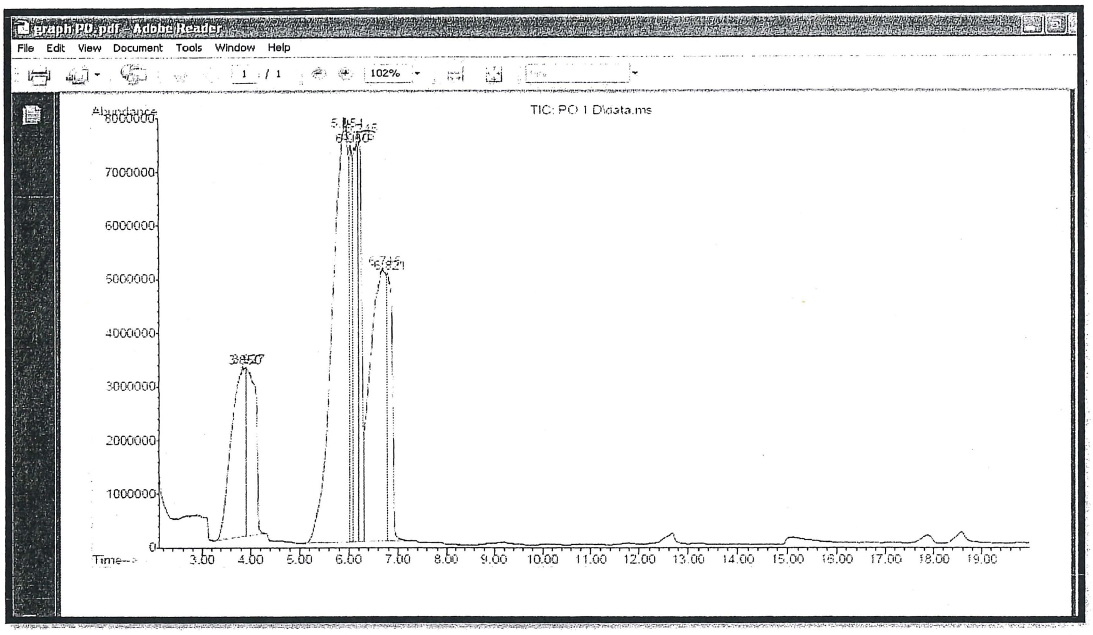
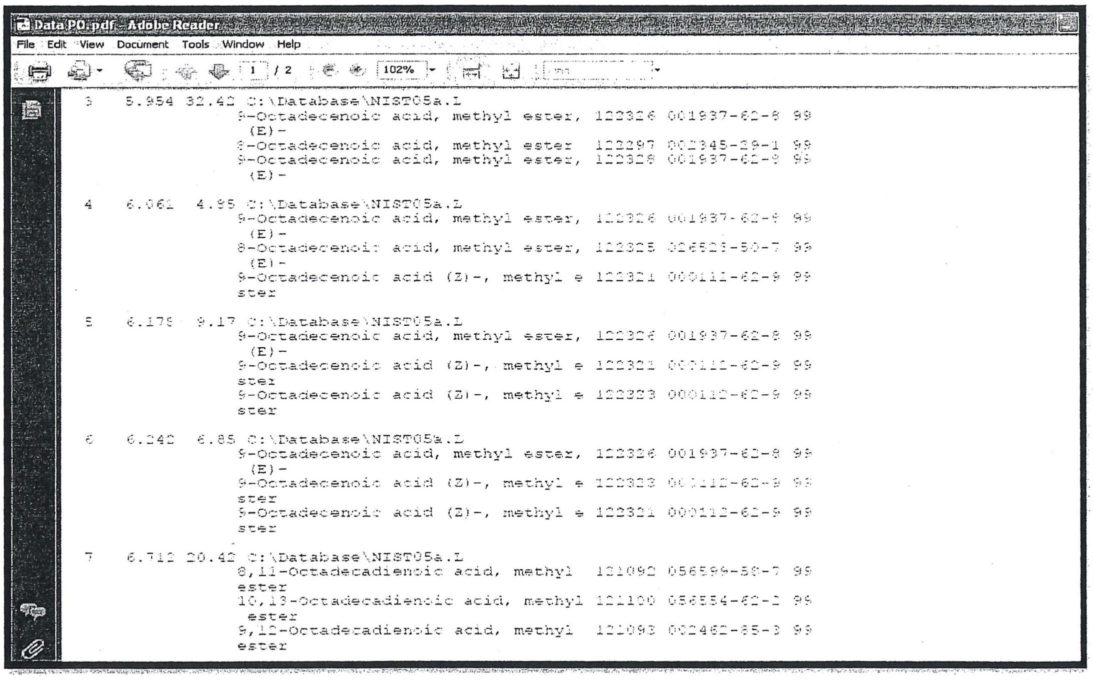
APPENDIX A

GRAPH AND DATA ANALYSIS

APPENDIX A1 (PRODUCT 0)





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                   (E)-

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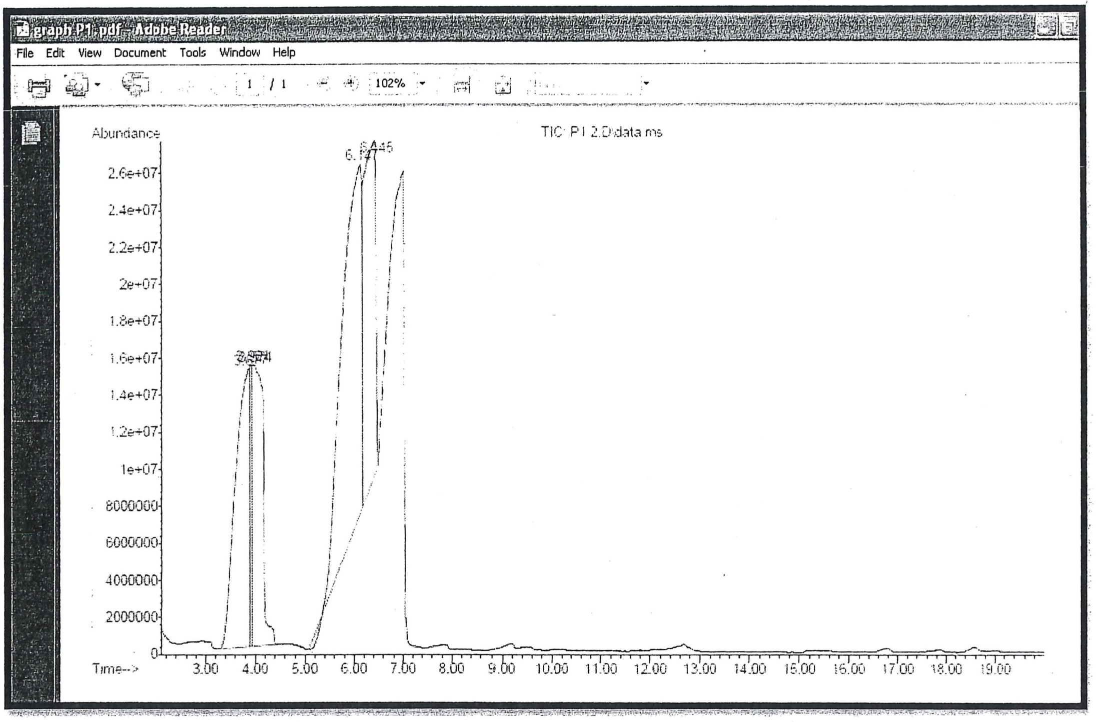
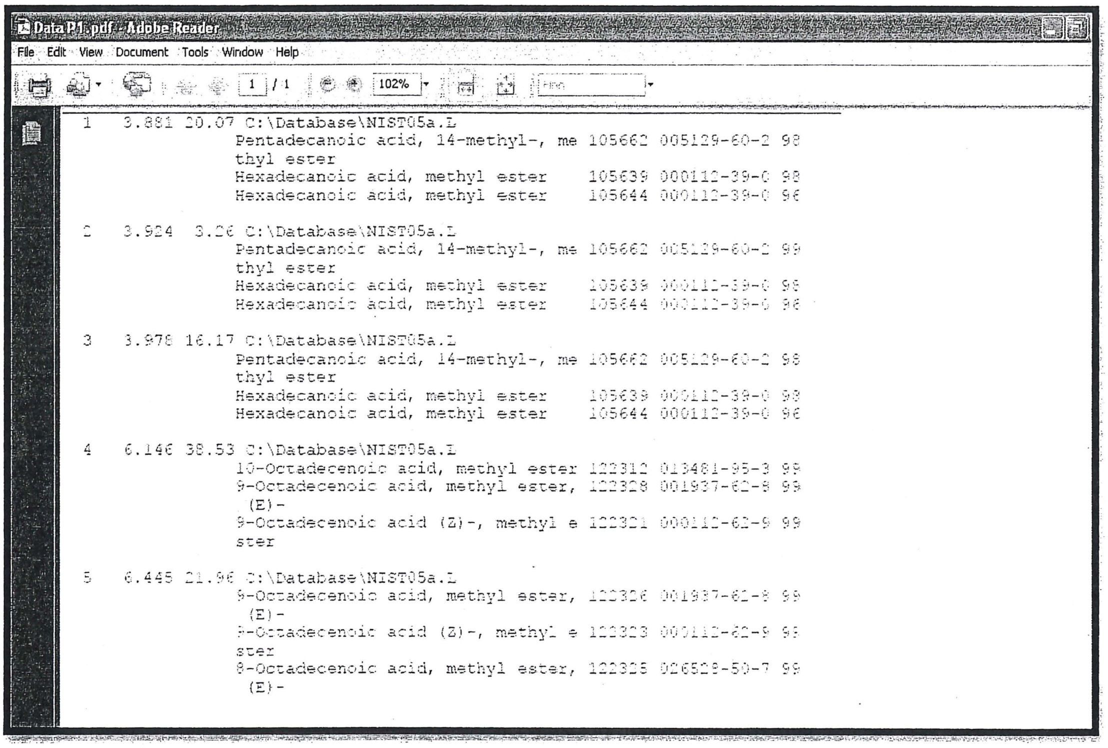
APPENDIX A2 (PRODUCT 1)





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                 Hexadecanoic acid, methyl ester    105644 000112-39-0 96

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                 ster

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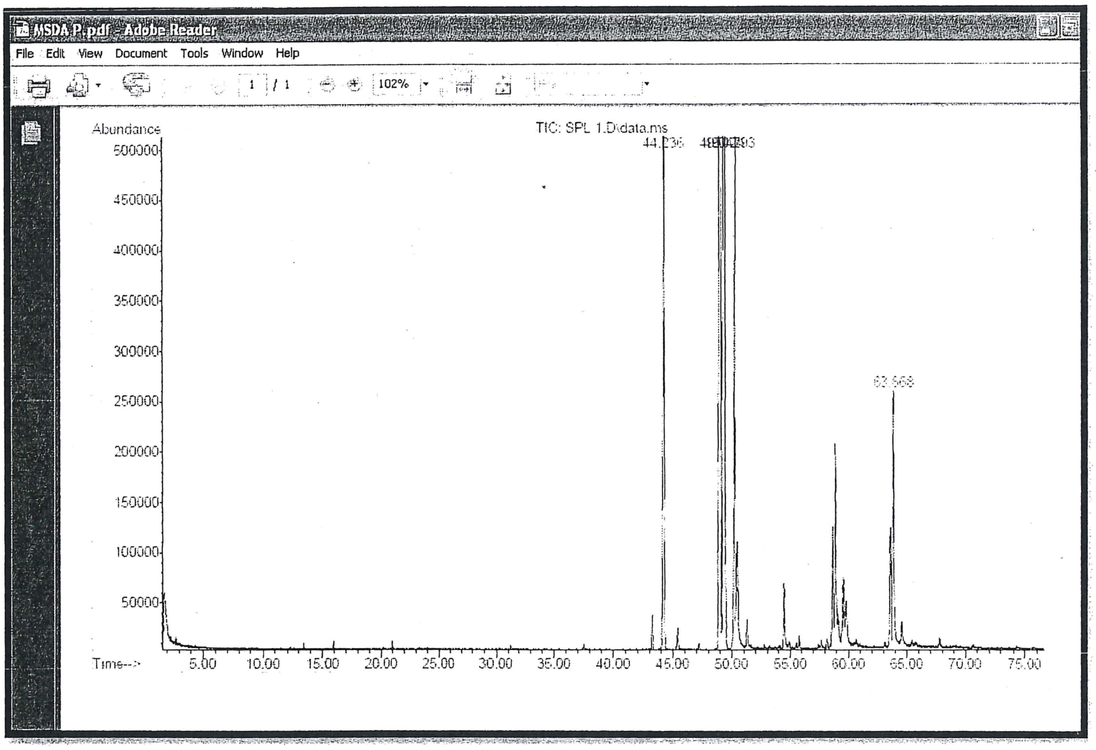

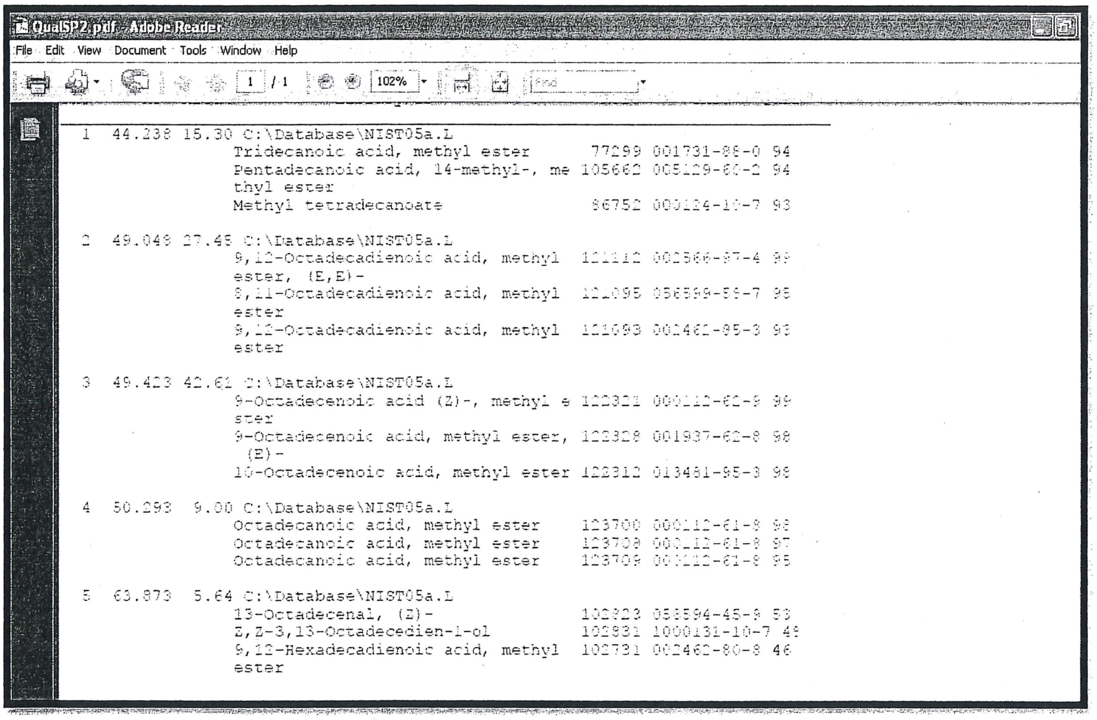

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                   ester
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                   ester

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                   ster
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                    (E)-
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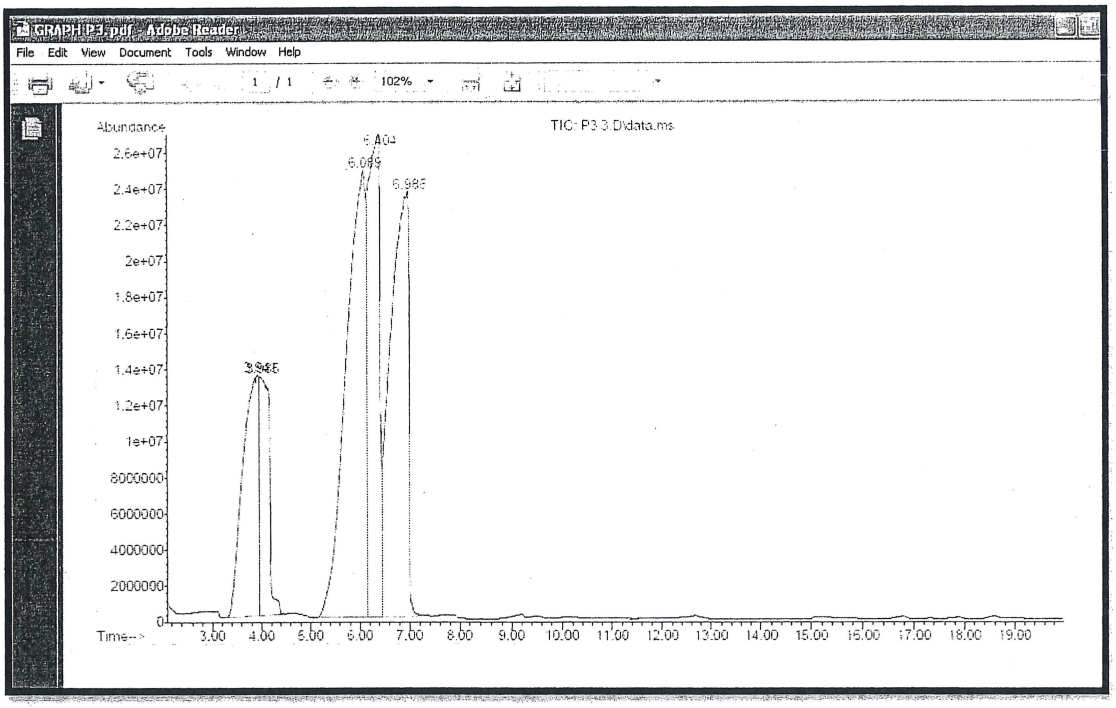
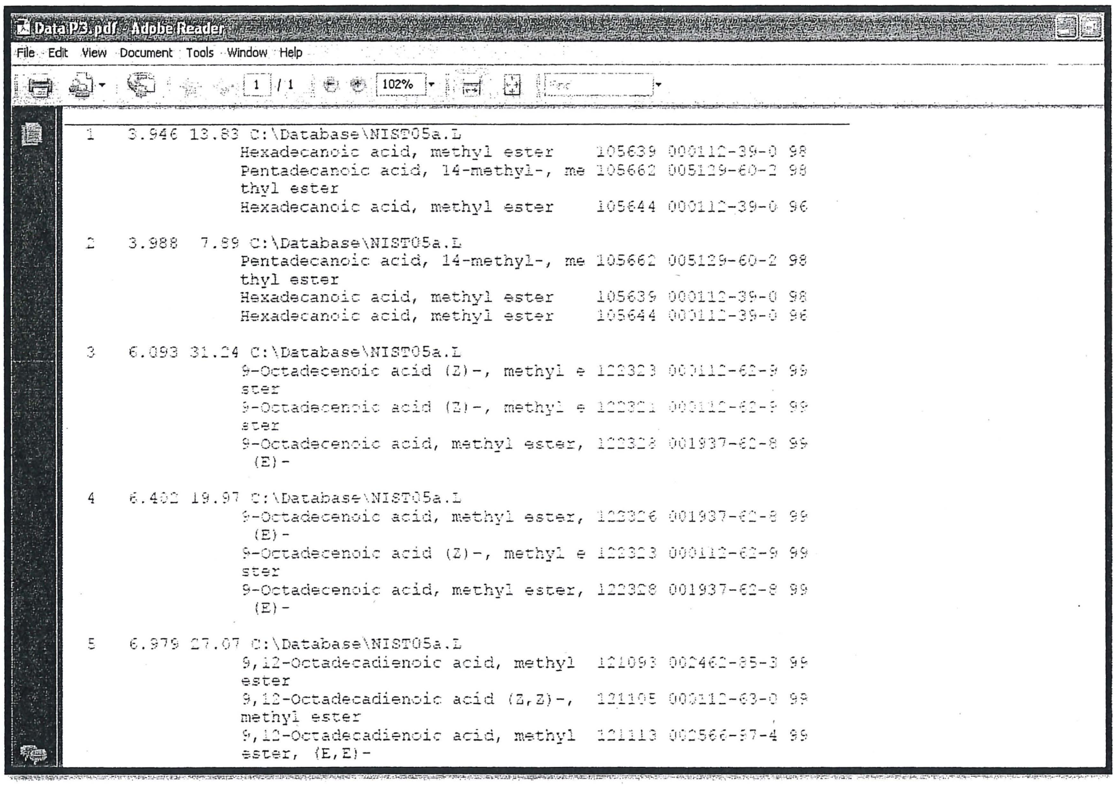
APPENDIX A4 (PRODUCT 3)





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                   (E)-

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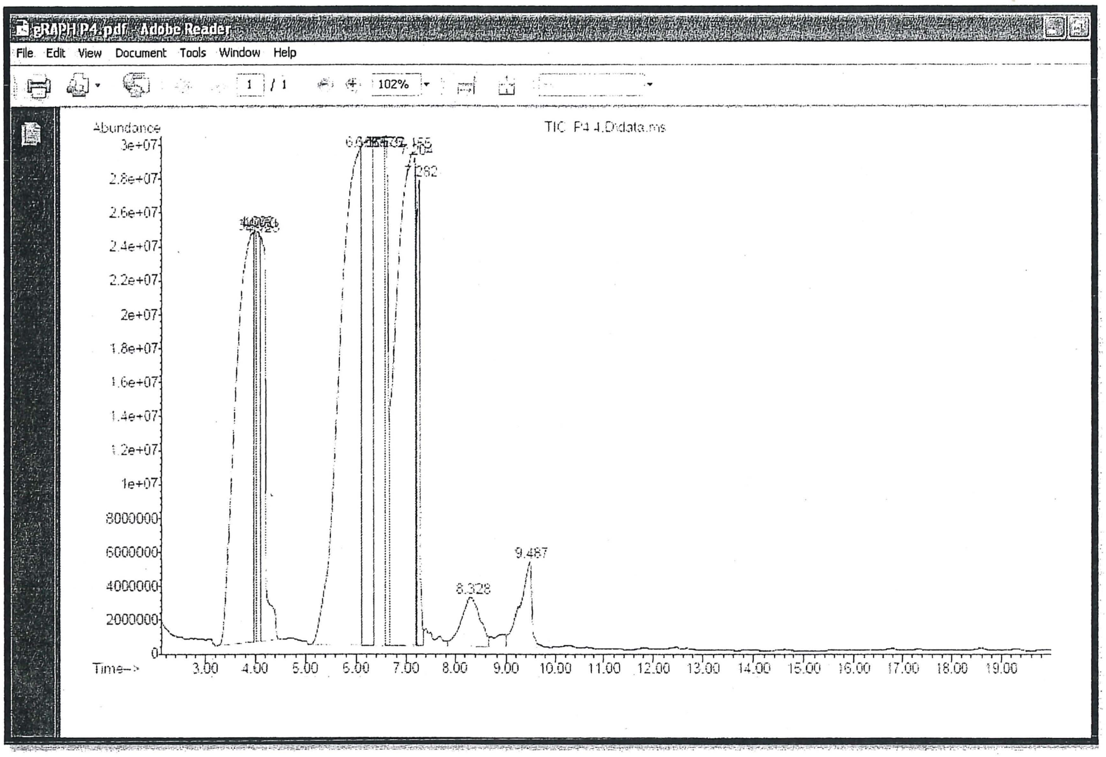

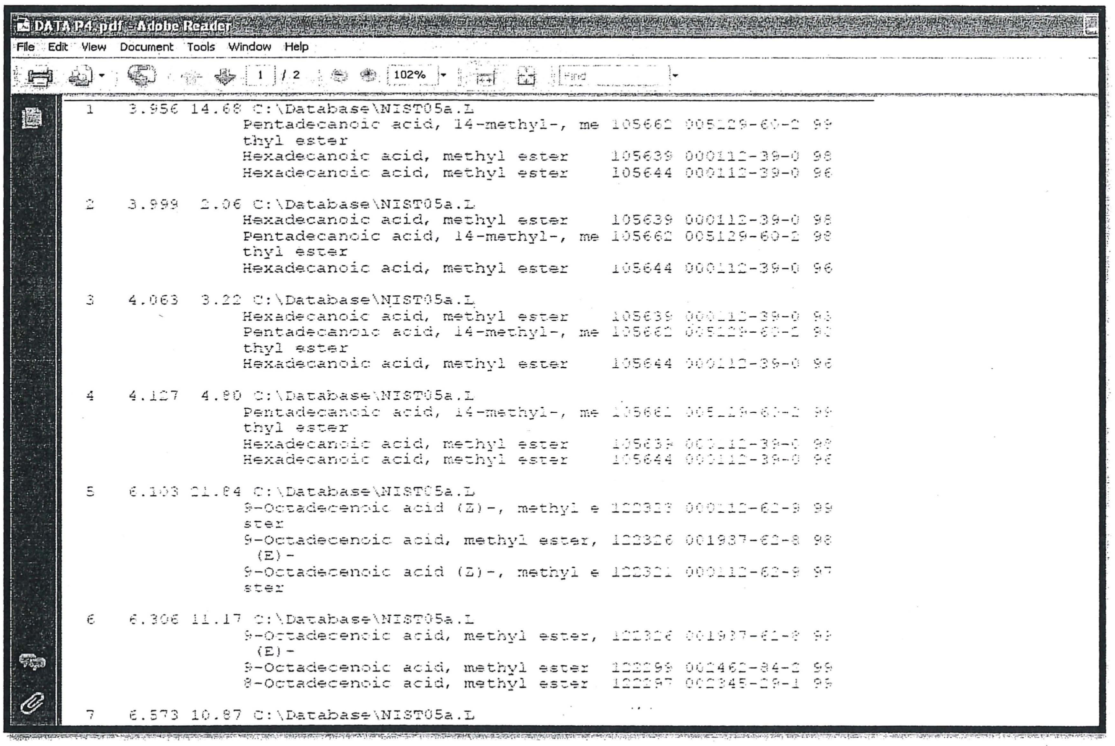

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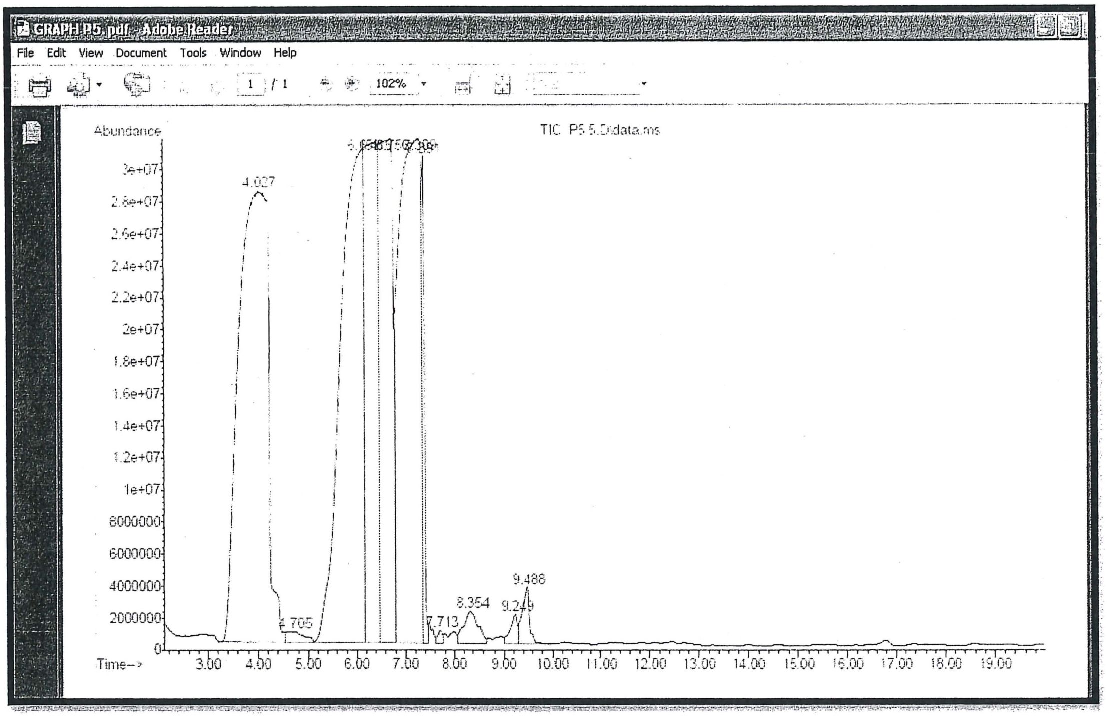

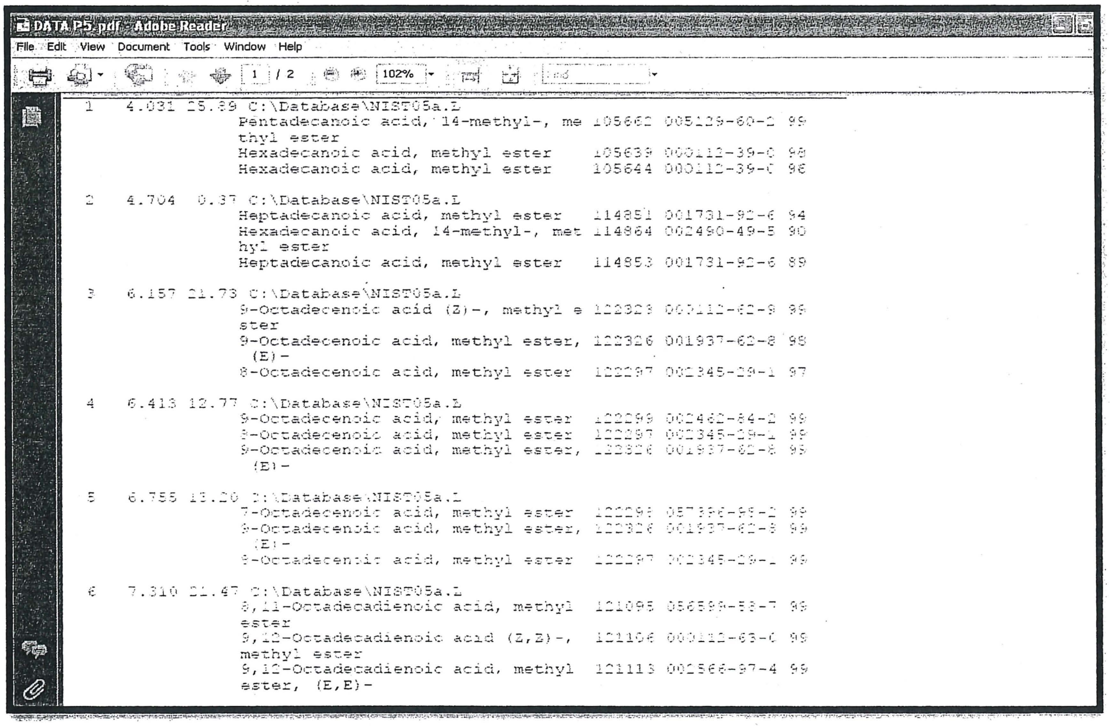

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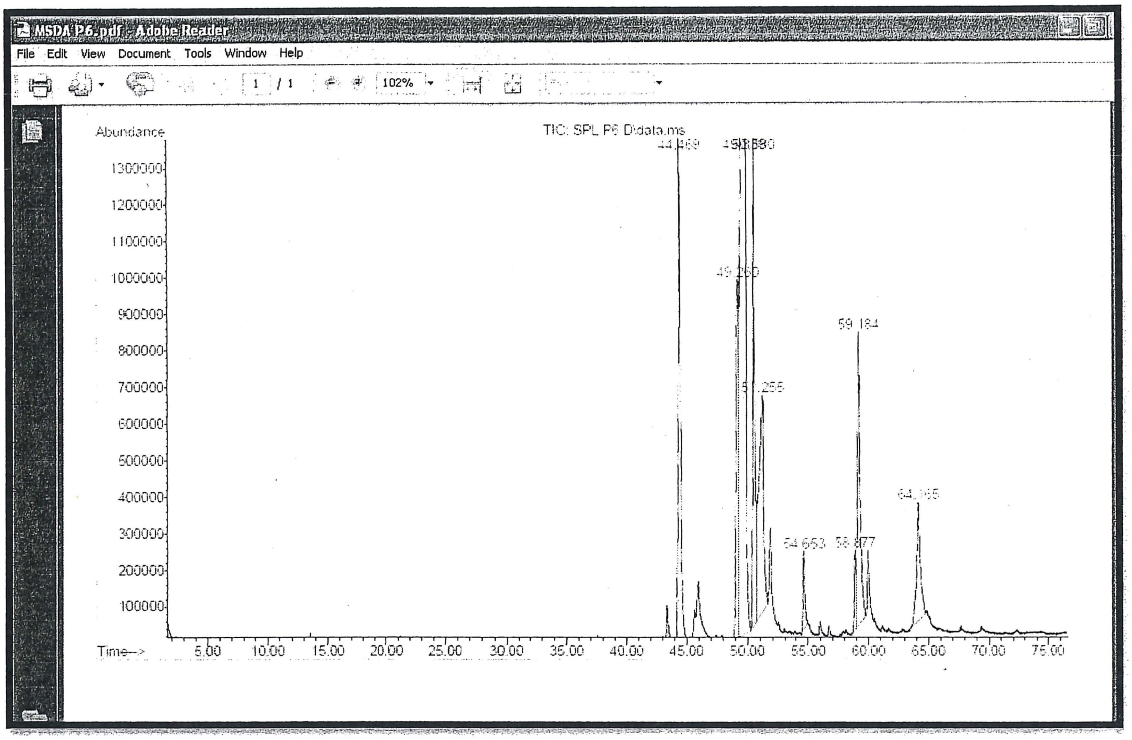

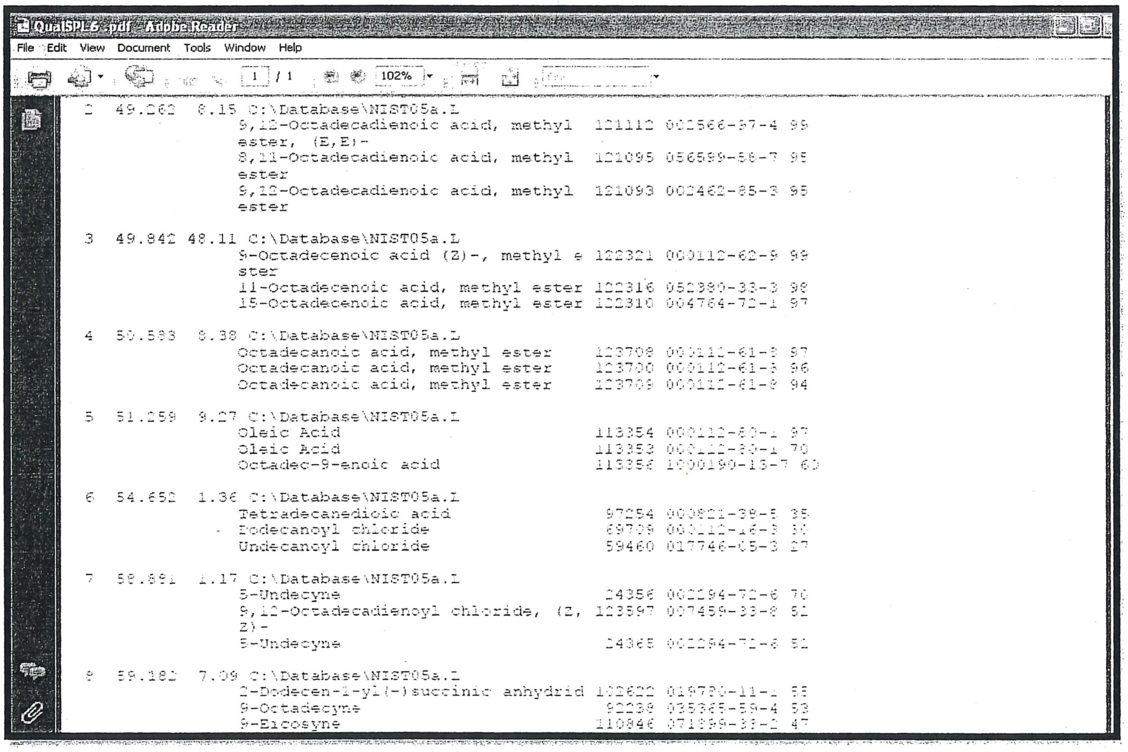

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                  ester

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                  Octadecanoic acid, methyl ester    123709 000112-61-8 94

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                  Oleic Acid                         113353 000112-80-1 70
                  Octadec-9-enoic acid               113356 1000190-13-7 60

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                  Z)-
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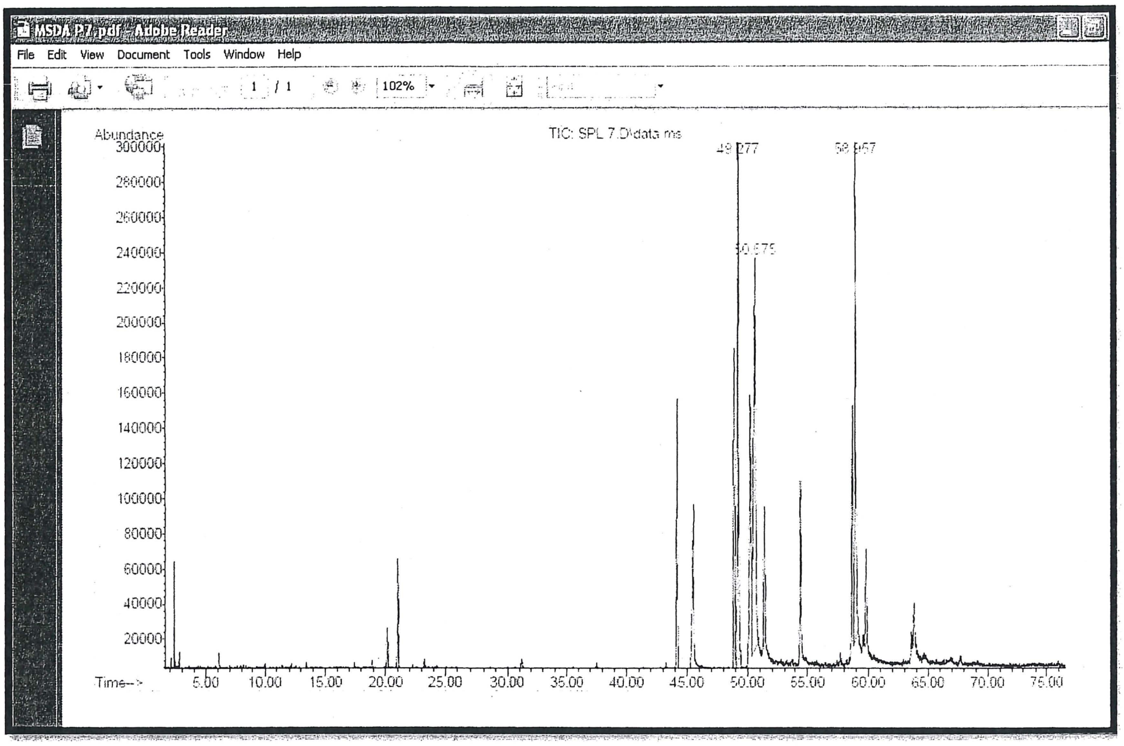

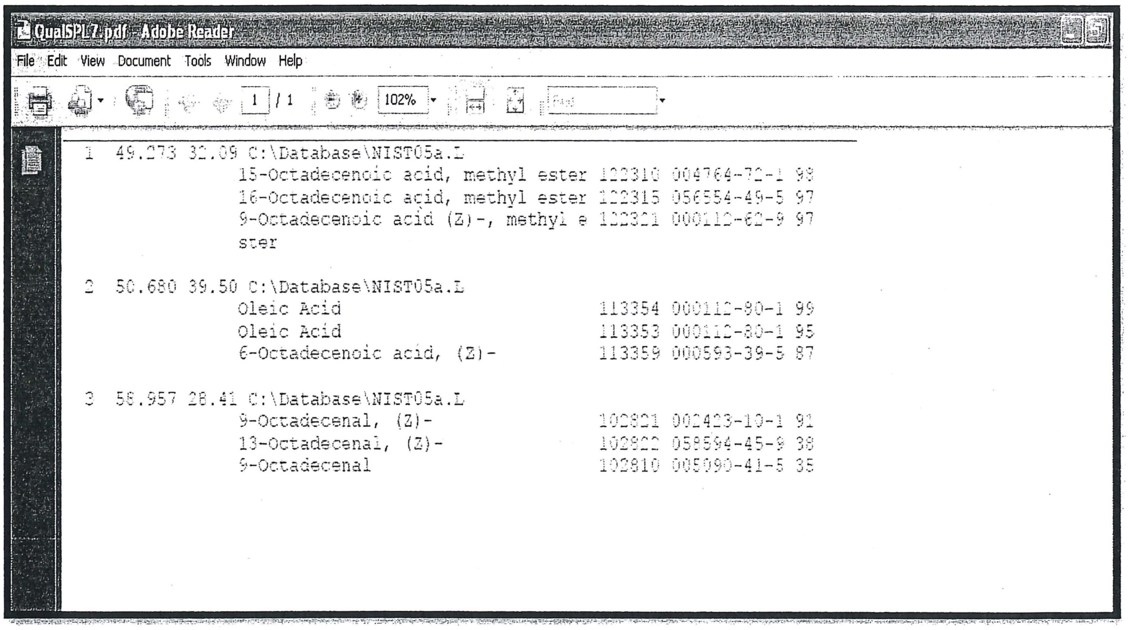

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               ster

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               Oleic Acid                         113353 000112-80-1 95
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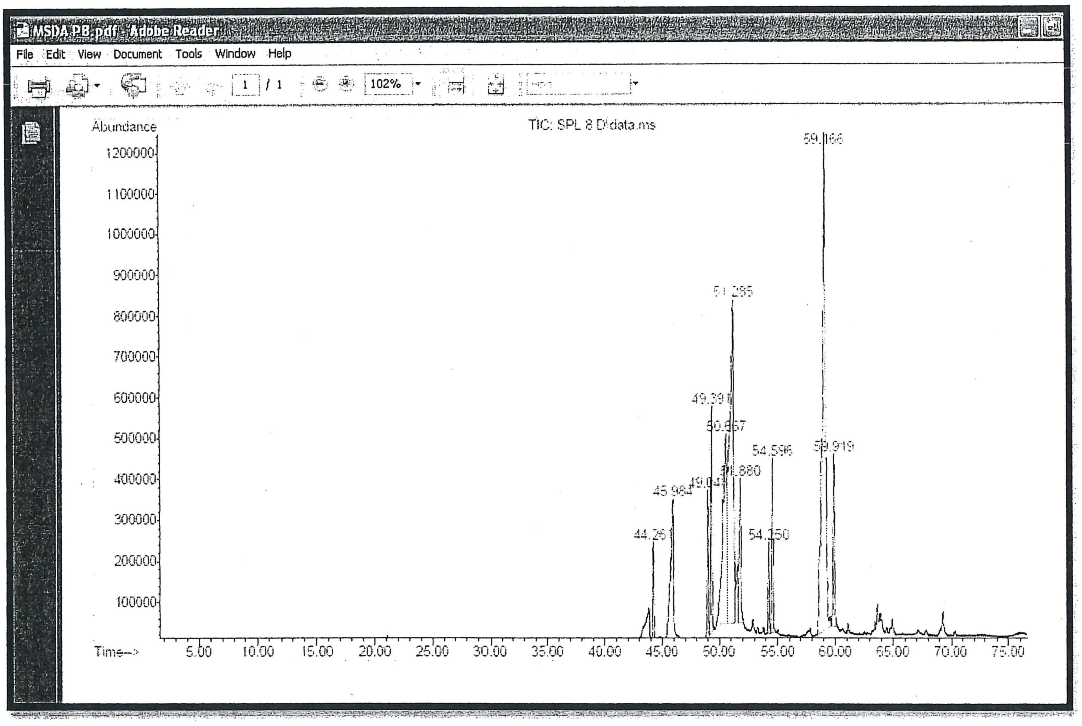

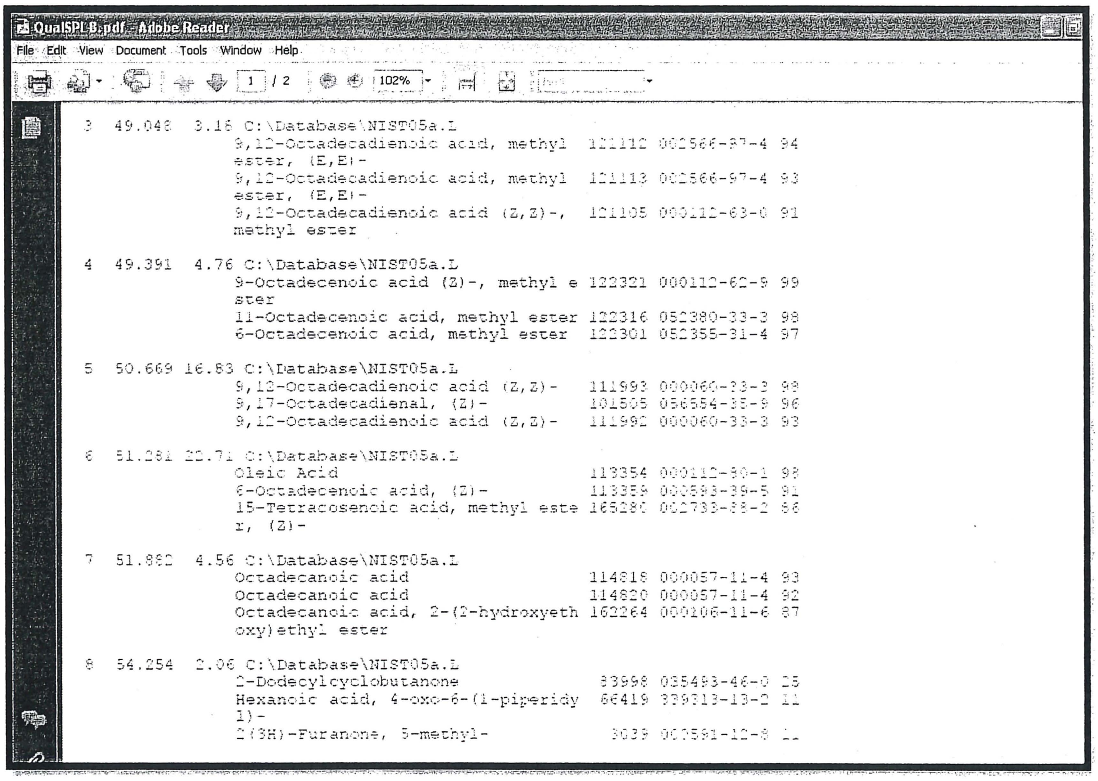

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3  49.048  3.16 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 94
                ester, (E,E)-
                9,12-Octadecadienoic acid, methyl  121113 002566-97-4 93
                ester, (E,E)-
                9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 91
                methyl ester

4  49.391  4.76 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                ster
                11-Octadecenoic acid, methyl ester 122316 052380-33-3 98
                6-Octadecenoic acid, methyl ester  122301 052355-31-4 97

5  50.669 16.83 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid (Z,Z)-   111993 000060-33-3 99
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 96
                9,12-Octadecadienoic acid (Z,Z)-   111992 000060-33-3 93

6  51.281 22.71 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 98
                6-Octadecenoic acid, (Z)-          113359 000593-39-5 91
                15-Tetracosenoic acid, methyl este 165280 002733-88-2 86
                r, (Z)-

7  51.882  4.56 C:\Database\NIST05a.L
                Octadecanoic acid                  114818 000057-11-4 93
                Octadecanoic acid                  114820 000057-11-4 92
                Octadecanoic acid, 2-(2-hydroxyeth 162264 000106-11-6 87
                oxy)ethyl ester

8  54.254  2.06 C:\Database\NIST05a.L
                2-Dodecylcyclobutanone              83998 035493-46-0 25
                Hexanoic acid, 4-oxo-6-(1-piperidy  66419 339313-13-2 11
                1)-
                2(3H)-Furanone, 5-methyl-            3039 000591-12-8 11
```
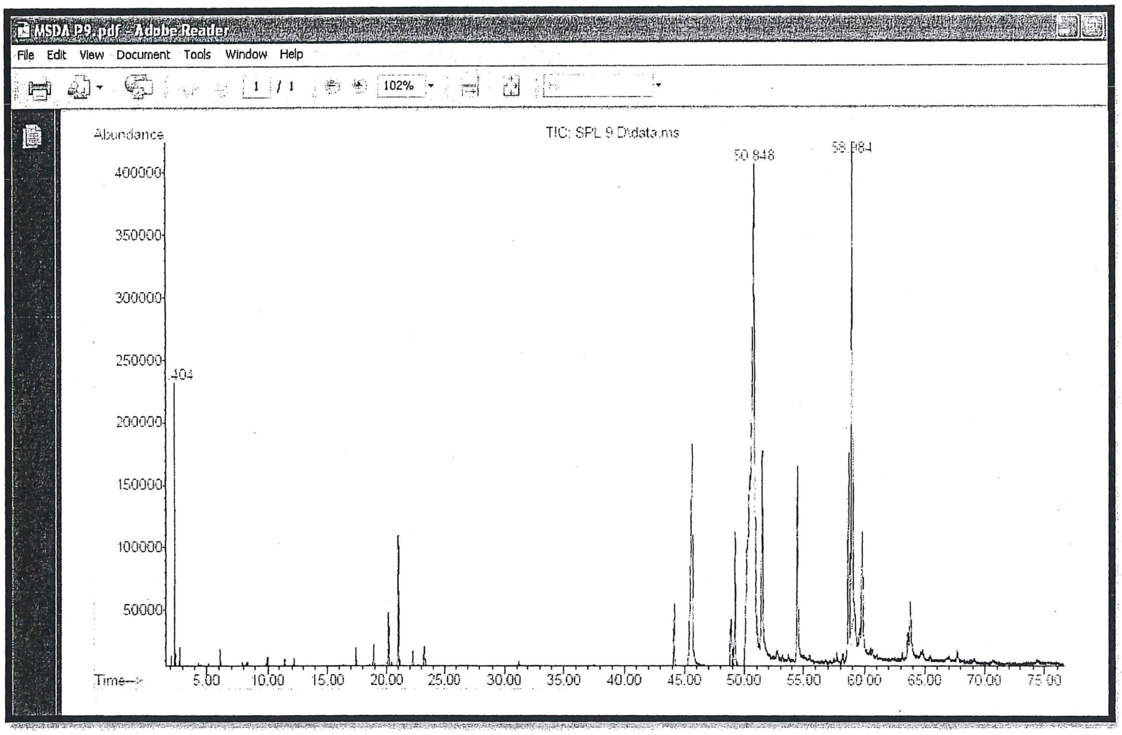
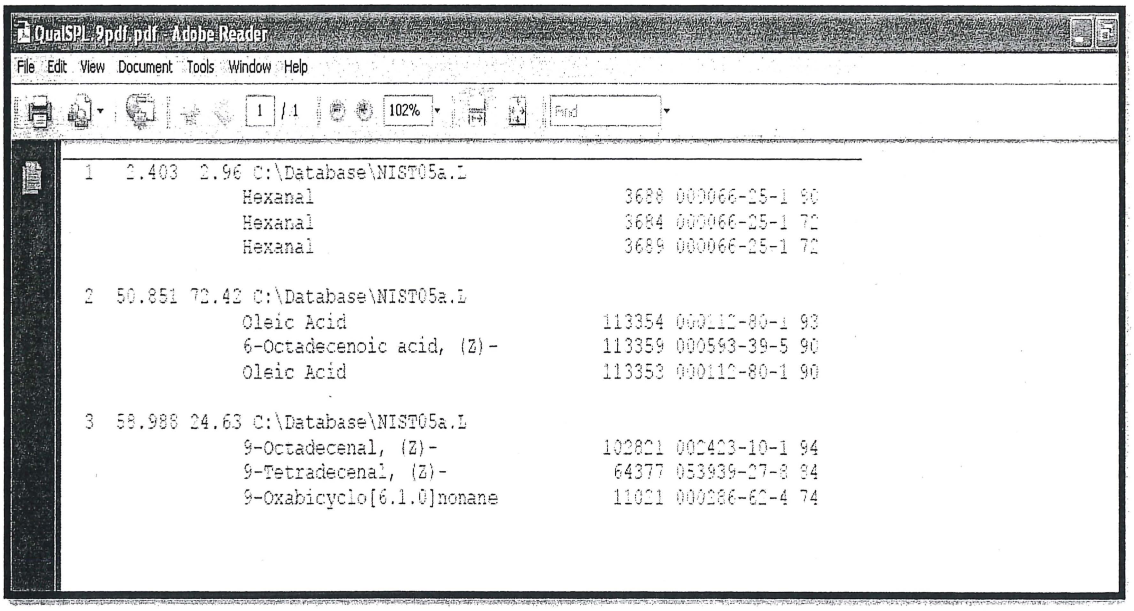

APPENDIX A 10 (PRODUCT 9)





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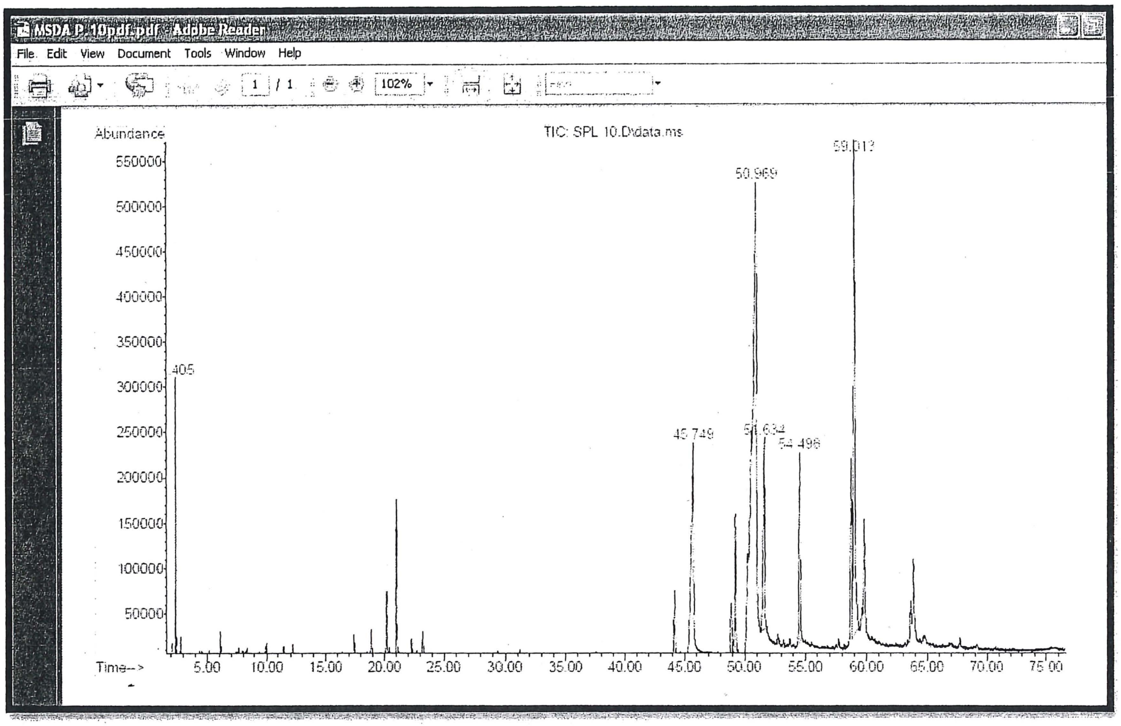
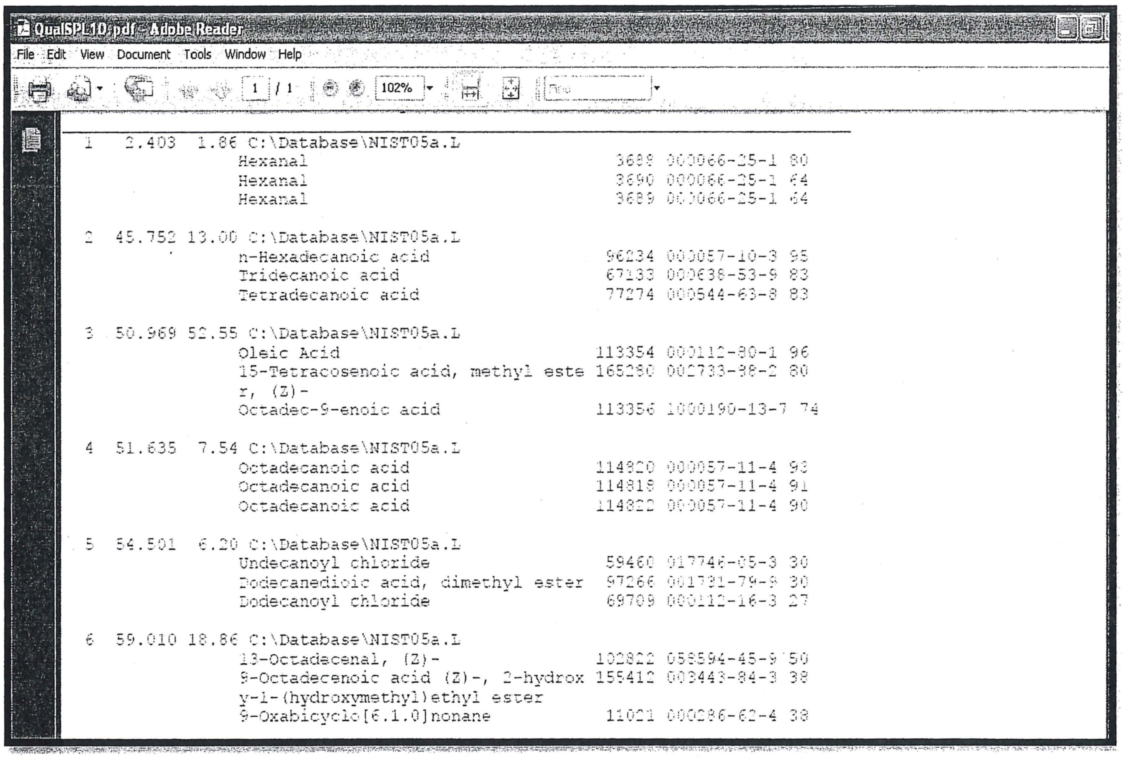
1   2.403  2.96 C:\Database\NIST05a.L
                 Hexanal                               3688 000066-25-1 90
                 Hexanal                               3684 000066-25-1 72
                 Hexanal                               3689 000066-25-1 72

2  50.851 72.42 C:\Database\NIST05a.L
                 Oleic Acid                          113354 000112-80-1 93
                 6-Octadecenoic acid, (Z)-           113359 000593-39-5 90
                 Oleic Acid                          113353 000112-80-1 90

3  58.988 24.63 C:\Database\NIST05a.L
                 9-Octadecenal, (Z)-                 102821 002423-10-1 94
                 9-Tetradecenal, (Z)-                 64377 053939-27-8 94
                 9-Oxabicyclo[6.1.0]nonane            11021 000286-62-4 74
```

APPPENDIX A11 (PRODUCT 10)





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1   2.403  1.86 C:\Database\NIST05a.L
               Hexanal                              3688 000066-25-1 80
               Hexanal                              3690 000066-25-1 64
               Hexanal                              3689 000066-25-1 64

2  45.752 13.00 C:\Database\NIST05a.L
               n-Hexadecanoic acid                 96234 000057-10-3 95
               Tridecanoic acid                    67133 000638-53-9 83
               Tetradecanoic acid                  77274 000544-63-8 83

3  50.969 52.55 C:\Database\NIST05a.L
               Oleic Acid                         113354 000112-80-1 96
               15-Tetracosenoic acid, methyl este 165280 002733-88-2 80
               r, (Z)-
               Octadec-9-enoic acid               113356 1000190-13-7 74

4  51.635  7.54 C:\Database\NIST05a.L
               Octadecanoic acid                  114820 000057-11-4 93
               Octadecanoic acid                  114818 000057-11-4 91
               Octadecanoic acid                  114822 000057-11-4 90

5  54.501  6.20 C:\Database\NIST05a.L
               Undecanoyl chloride                 59460 017746-05-3 30
               Dodecanedioic acid, dimethyl ester  97266 001731-79-9 30
               Dodecanoyl chloride                 69709 000112-16-3 27

6  59.010 18.86 C:\Database\NIST05a.L
               13-Octadecenal, (Z)-               102822 058594-45-9 50
               9-Octadecenoic acid (Z)-, 2-hydrox 155412 003443-84-3 38
               y-1-(hydroxymethyl)ethyl ester
               9-Oxabicyclo[6.1.0]nonane           11021 000286-62-4 38
```
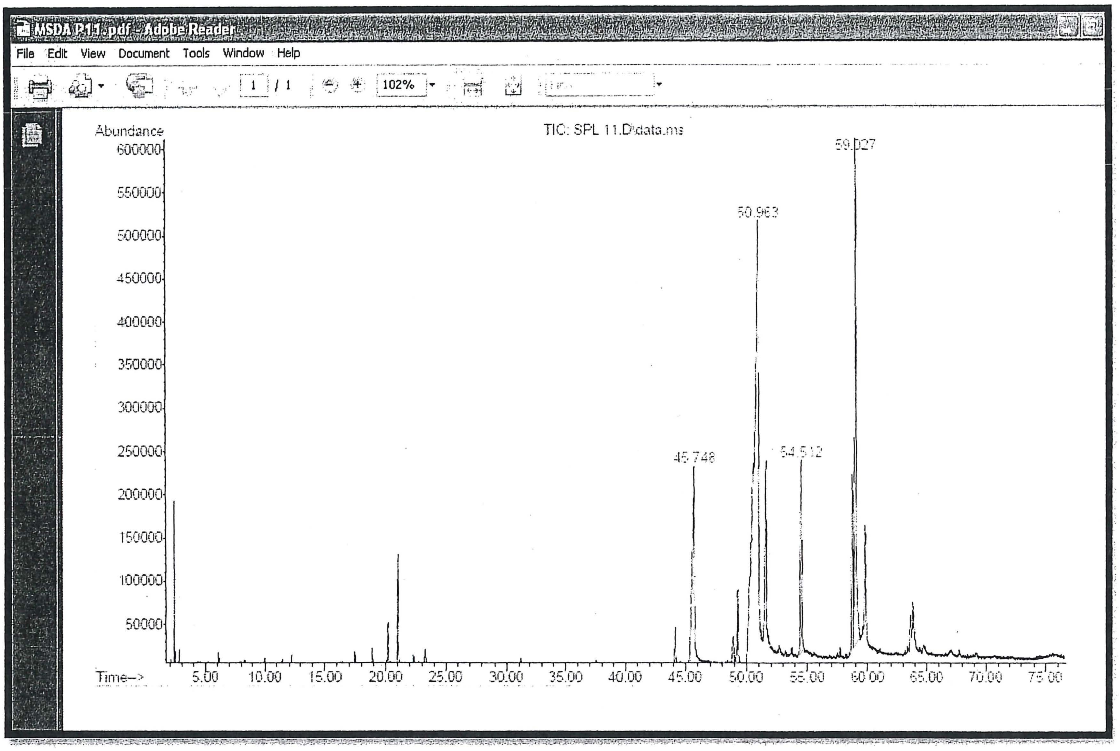
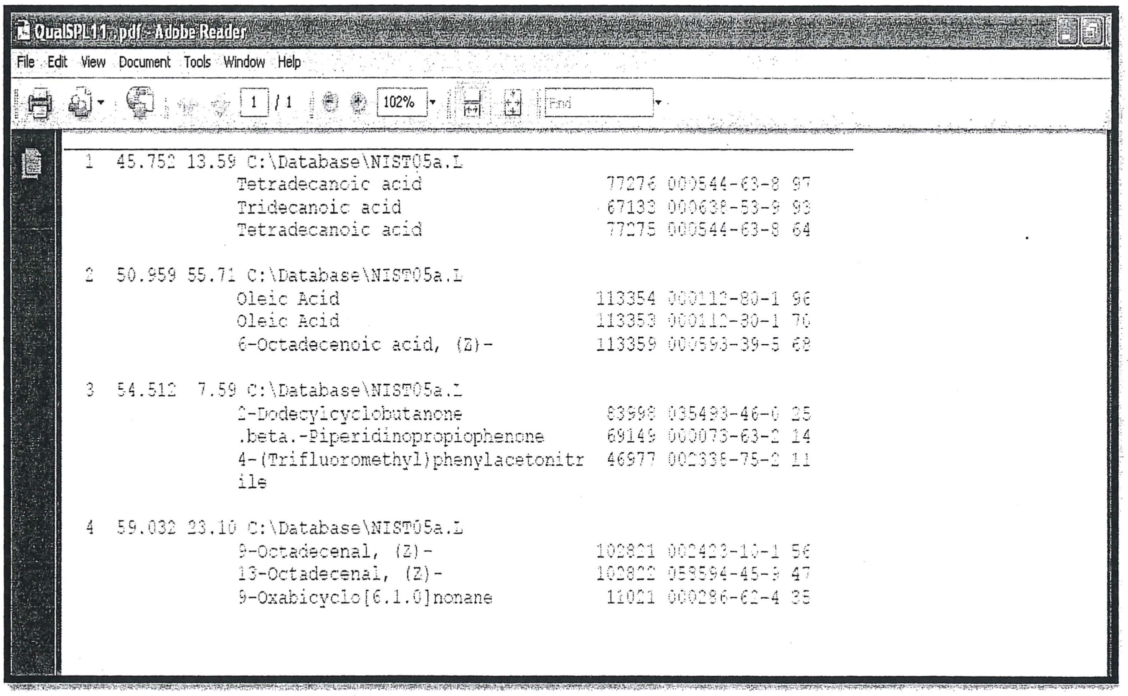

APPENDIX A 12 (PRODUCT 11)





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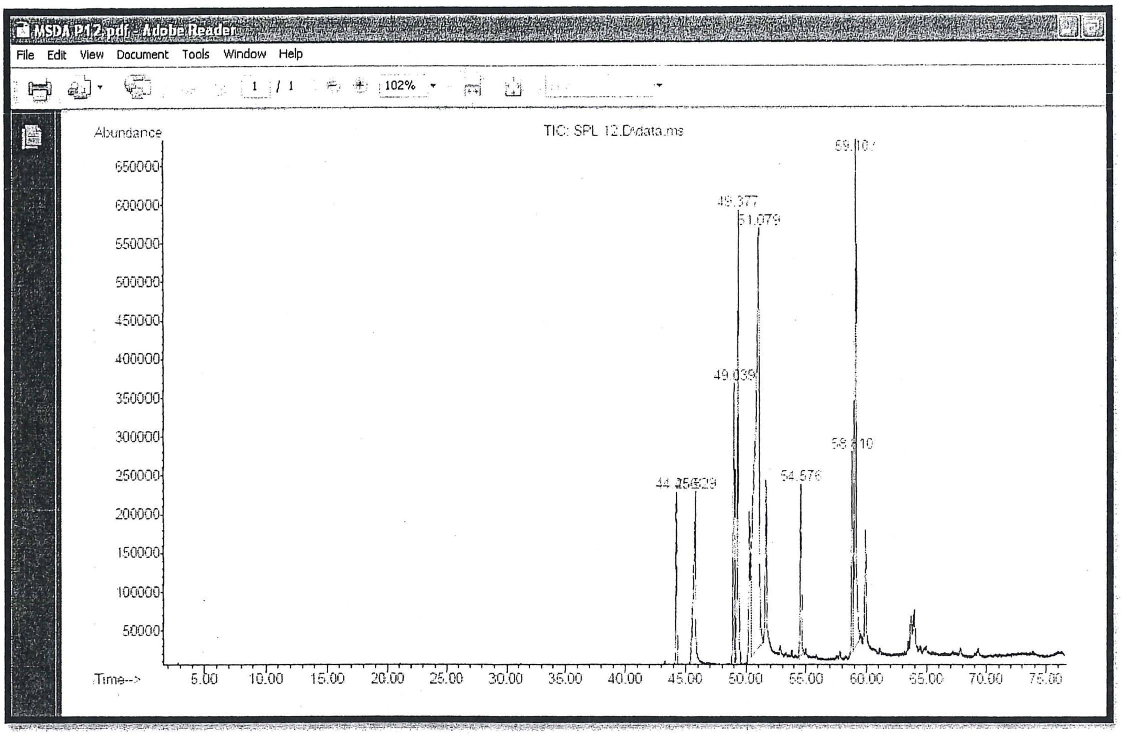
1  45.752 13.59 C:\Database\NIST05a.L
                Tetradecanoic acid                 77276 000544-63-8 97
                Tridecanoic acid                   67133 000638-53-9 93
                Tetradecanoic acid                 77275 000544-63-8 64

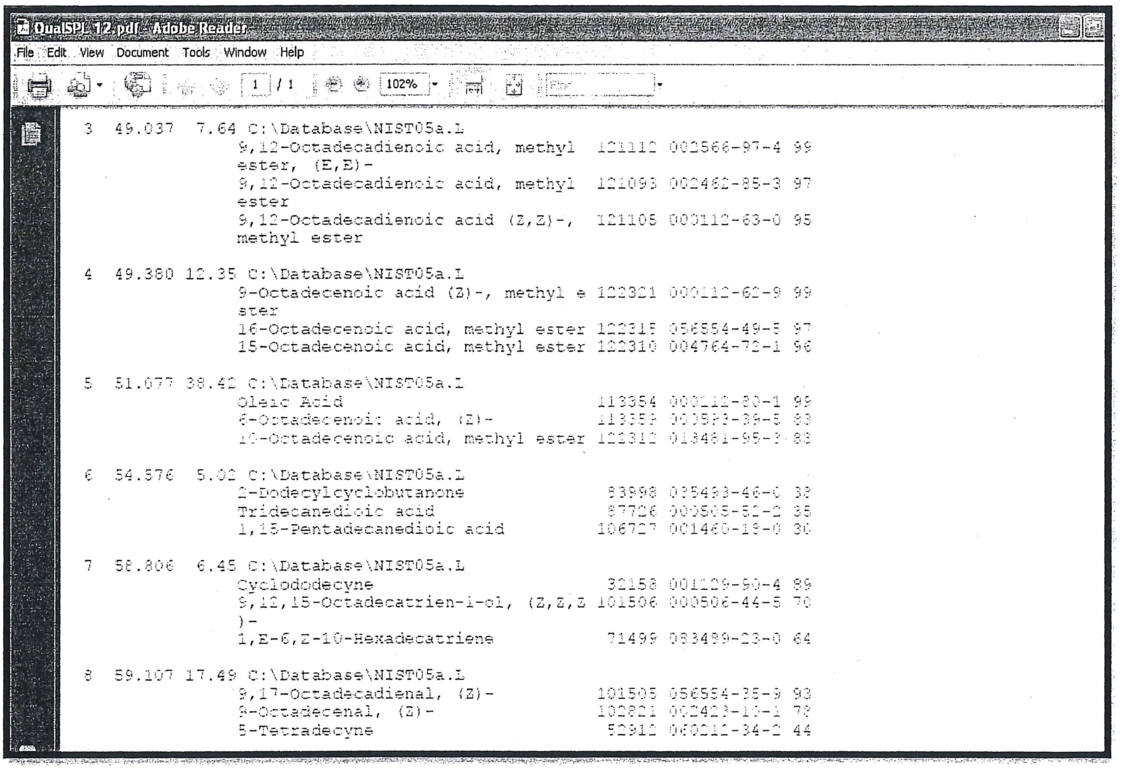
2  50.959 55.71 C:\Database\NIST05a.L
                Oleic Acid                        113354 000112-80-1 96
                Oleic Acid                        113353 000112-80-1 70
                6-Octadecenoic acid, (Z)-         113359 000593-39-5 68

3  54.512  7.59 C:\Database\NIST05a.L
                2-Dodecylcyclobutanone             83998 035493-46-0 25
                .beta.-Piperidinopropiophenone     69149 000073-63-2 14
                4-(Trifluoromethyl)phenylacetonitr  46977 002338-75-2 11
                ile

4  59.032 23.10 C:\Database\NIST05a.L
                9-Octadecenal, (Z)-               102821 002423-10-1 56
                13-Octadecenal, (Z)-              102822 058594-45-9 47
                9-Oxabicyclo[6.1.0]nonane          11021 000286-62-4 35
```

APPENDIX A13 (PRODUCT 12)





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                 9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
                 ester, (E,E)-
                 9,12-Octadecadienoic acid, methyl  121093 002462-85-3 97
                 ester
                 9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 95
                 methyl ester

4  49.380 12.35 C:\Database\NIST05a.L
                 9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                 ster
                 16-Octadecenoic acid, methyl ester 122315 056554-49-5 97
                 15-Octadecenoic acid, methyl ester 122310 004764-72-1 96

5  51.077 38.42 C:\Database\NIST05a.L
                 Oleic Acid                         113354 000112-80-1 99
                 6-Octadecenoic acid, (Z)-          113359 000593-39-5 83
                 10-Octadecenoic acid, methyl ester 122312 013481-95-3 83

6  54.576  5.02 C:\Database\NIST05a.L
                 2-Dodecylcyclobutanone              83998 035493-46-0 38
                 Tridecanedioic acid                 87726 000505-52-2 35
                 1,15-Pentadecanedioic acid         106727 001460-18-0 30

7  58.806  6.45 C:\Database\NIST05a.L
                 Cyclododecyne                       32158 001129-90-4 89
                 9,12,15-Octadecatrien-1-ol, (Z,Z,Z 101506 000506-44-5 70
                 )-
                 1,E-6,Z-10-Hexadecatriene           71499 083489-23-0 64

8  59.107 17.49 C:\Database\NIST05a.L
                 9,17-Octadecadienal, (Z)-          101505 056554-35-9 93
                 9-Octadecenal, (Z)-                102821 002423-10-1 78
                 5-Tetradecyne                       52912 060212-34-2 44
```
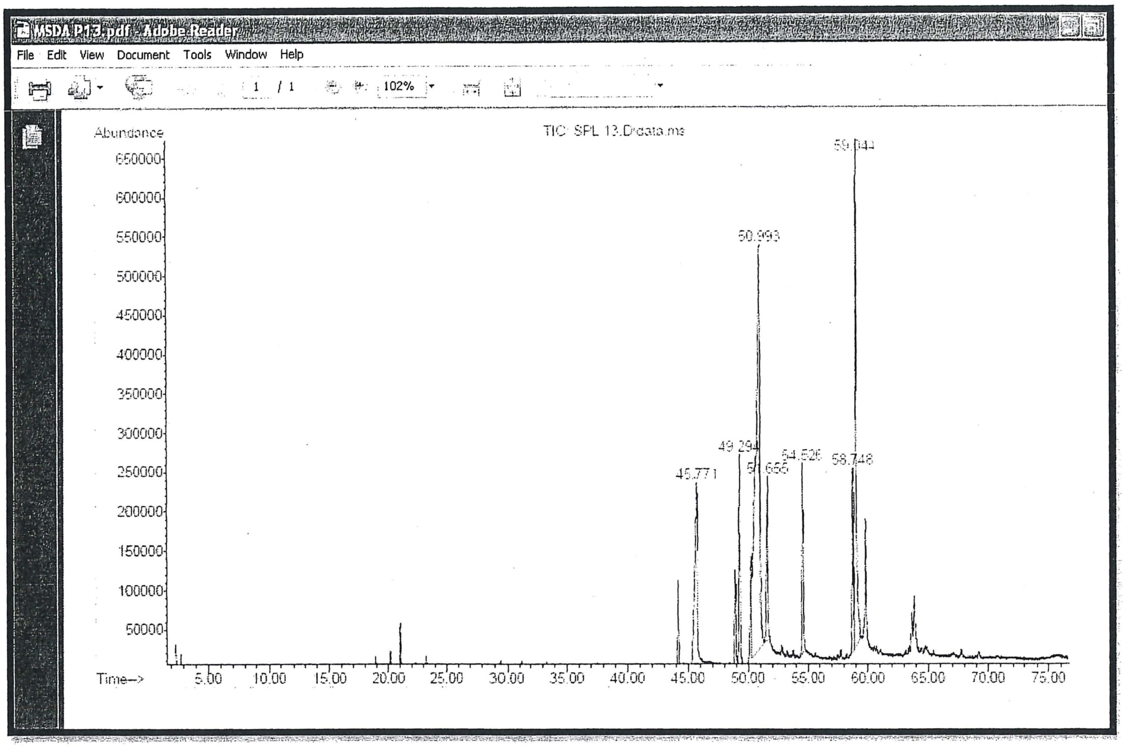
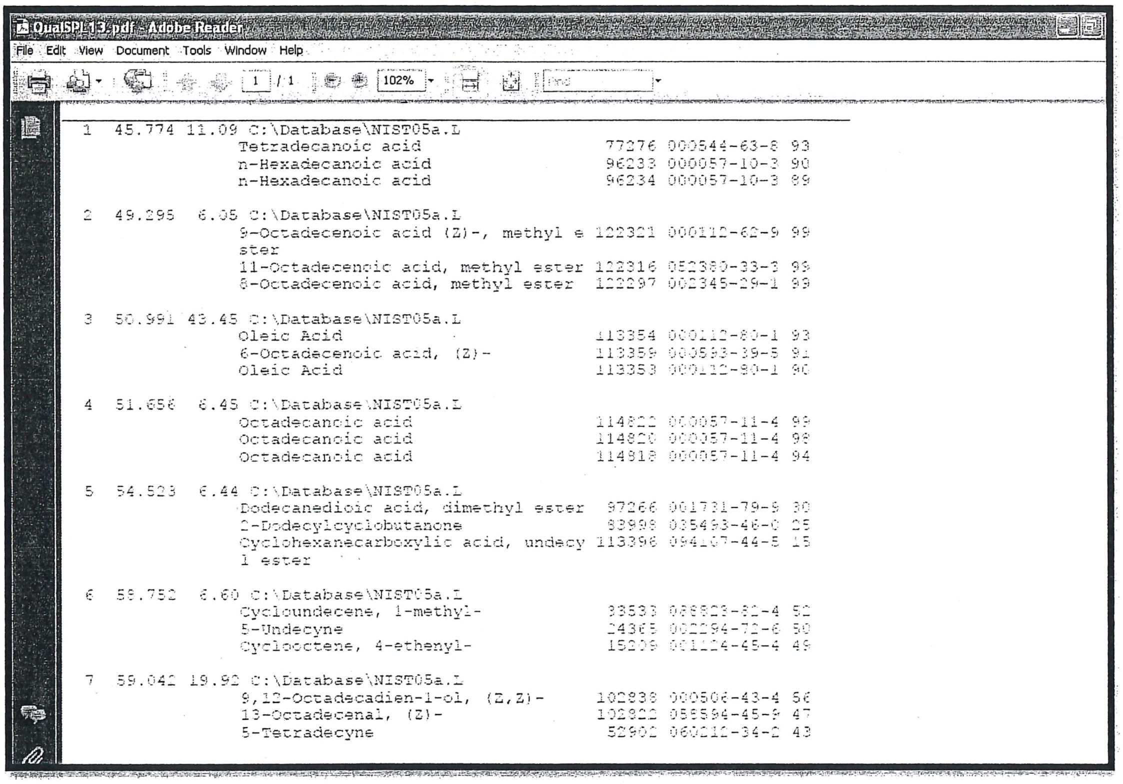

APPENDIX A 14 (PRODUCT 13)





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  1   45.774 11.09 C:\Database\NIST05a.L
                   Tetradecanoic acid                  77276 000544-63-8 93
                   n-Hexadecanoic acid                 96233 000057-10-3 90
                   n-Hexadecanoic acid                 96234 000057-10-3 89

  2   49.295  6.05 C:\Database\NIST05a.L
                   9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                   ster
                   11-Octadecenoic acid, methyl ester 122316 052380-33-3 99
                   8-Octadecenoic acid, methyl ester  122297 002345-29-1 99

  3   50.991 43.45 C:\Database\NIST05a.L
                   Oleic Acid                         113354 000112-80-1 93
                   6-Octadecenoic acid, (Z)-          113359 000593-39-5 91
                   Oleic Acid                         113353 000112-80-1 90

  4   51.656  6.45 C:\Database\NIST05a.L
                   Octadecanoic acid                  114822 000057-11-4 99
                   Octadecanoic acid                  114820 000057-11-4 98
                   Octadecanoic acid                  114818 000057-11-4 94

  5   54.523  6.44 C:\Database\NIST05a.L
                   Dodecanedioic acid, dimethyl ester  97266 001731-79-9 30
                   2-Dodecylcyclobutanone              83999 035493-46-0 25
                   Cyclohexanecarboxylic acid, undecy 113396 094107-44-5 15
                   l ester

  6   58.752  6.60 C:\Database\NIST05a.L
                   Cycloundecene, 1-methyl-            33533 088823-82-4 52
                   5-Undecyne                          24365 002294-72-6 50
                   Cyclooctene, 4-ethenyl-             15209 001124-45-4 49

  7   59.042 19.92 C:\Database\NIST05a.L
                   9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 56
                   13-Octadecenal, (Z)-               102822 058594-45-9 47
                   5-Tetradecyne                       52902 060212-34-2 43
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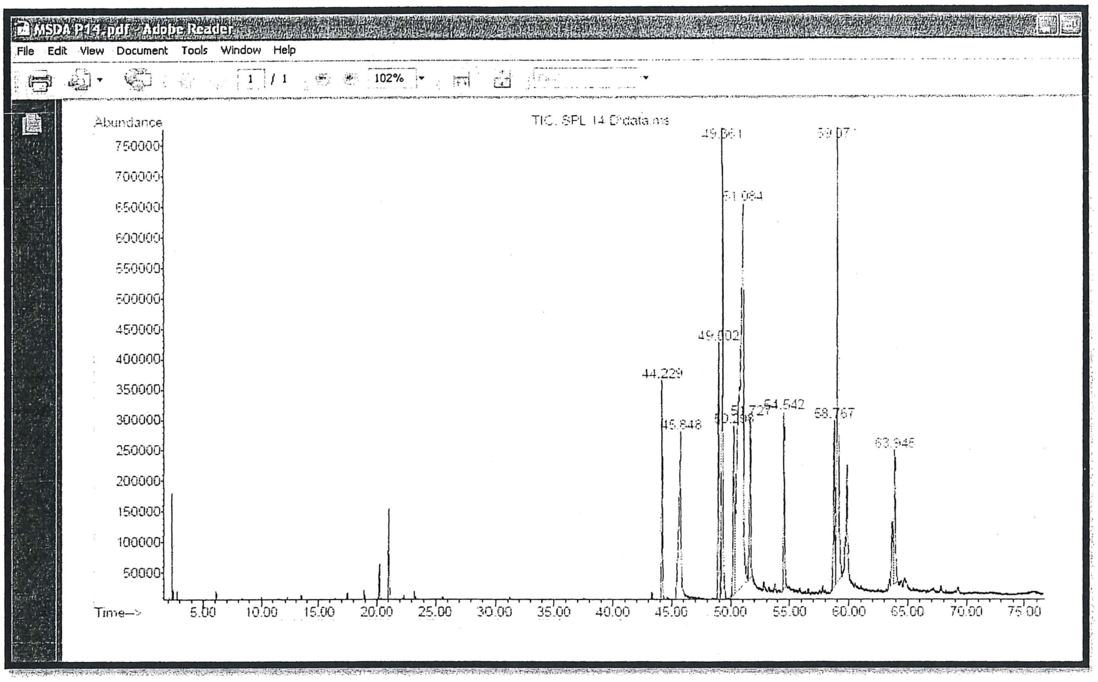
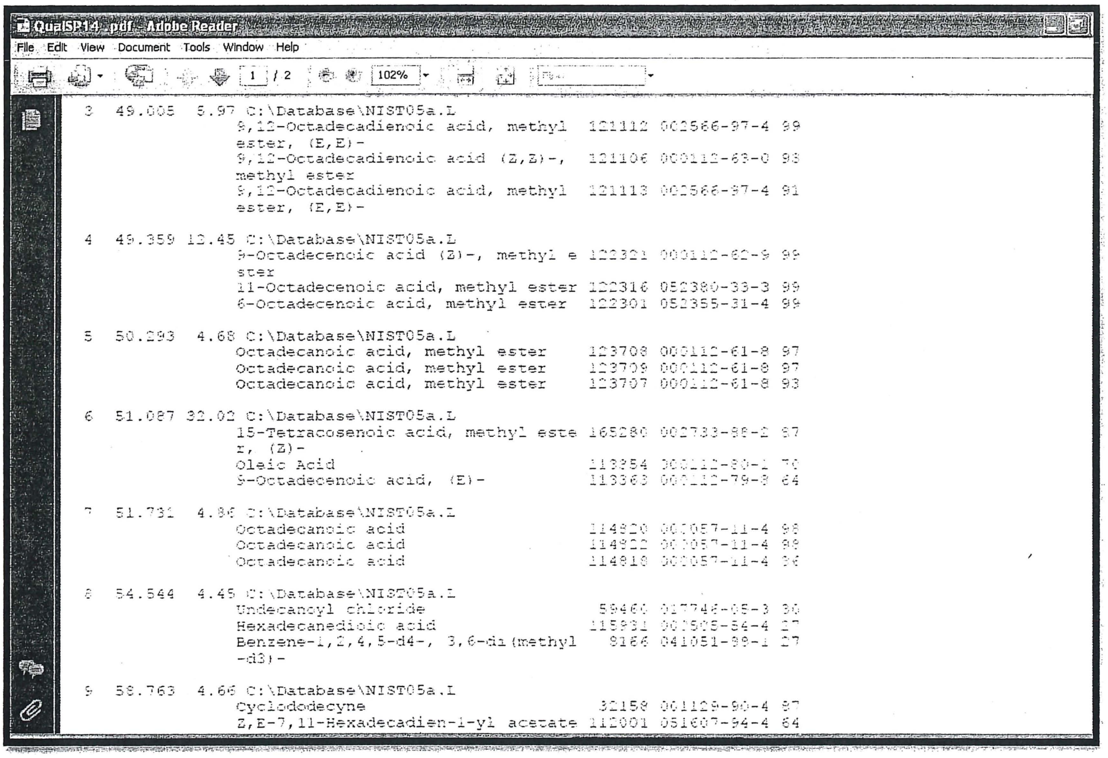
APPENDIX A 15 (PRODUCT 14)





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3   49.005  5.97 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
                 ester, (E,E)-
                 9,12-Octadecadienoic acid (Z,Z)-,  121106 000112-63-0 93
                 methyl ester
                 9,12-Octadecadienoic acid, methyl  121113 002566-97-4 91
                 ester, (E,E)-

4   49.359 12.45 C:\Database\NIST05a.L
                 9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                 ster
                 11-Octadecenoic acid, methyl ester 122316 052380-33-3 99
                 6-Octadecenoic acid, methyl ester  122301 052355-31-4 99

5   50.293  4.68 C:\Database\NIST05a.L
                 Octadecanoic acid, methyl ester    123708 000112-61-8 97
                 Octadecanoic acid, methyl ester    123709 000112-61-8 97
                 Octadecanoic acid, methyl ester    123707 000112-61-8 93

6   51.087 32.02 C:\Database\NIST05a.L
                 15-Tetracosenoic acid, methyl este 165280 002733-88-2 87
                 r, (Z)-
                 Oleic Acid                         113354 000112-80-1 70
                 9-Octadecenoic acid, (E)-          113363 000112-79-8 64

7   51.731  4.86 C:\Database\NIST05a.L
                 Octadecanoic acid                  114820 000057-11-4 98
                 Octadecanoic acid                  114822 000057-11-4 99
                 Octadecanoic acid                  114818 000057-11-4 96

8   54.544  4.45 C:\Database\NIST05a.L
                 Undecanoyl chloride                 59460 017746-05-3 30
                 Hexadecanedioic acid               115931 000505-54-4 27
                 Benzene-1,2,4,5-d4-, 3,6-di(methyl   8166 041051-88-1 27
                 -d3)-

9   58.763  4.66 C:\Database\NIST05a.L
                 Cyclododecyne                       32158 001129-90-4 87
                 Z,E-7,11-Hexadecadien-1-yl acetate 112001 051607-94-4 64
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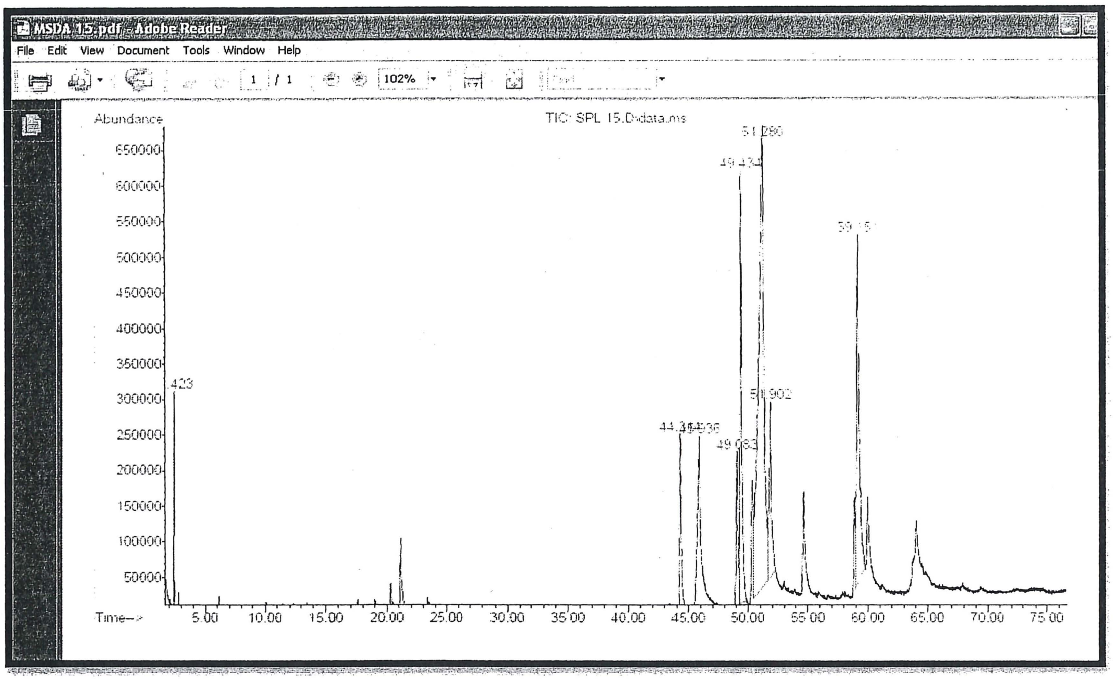
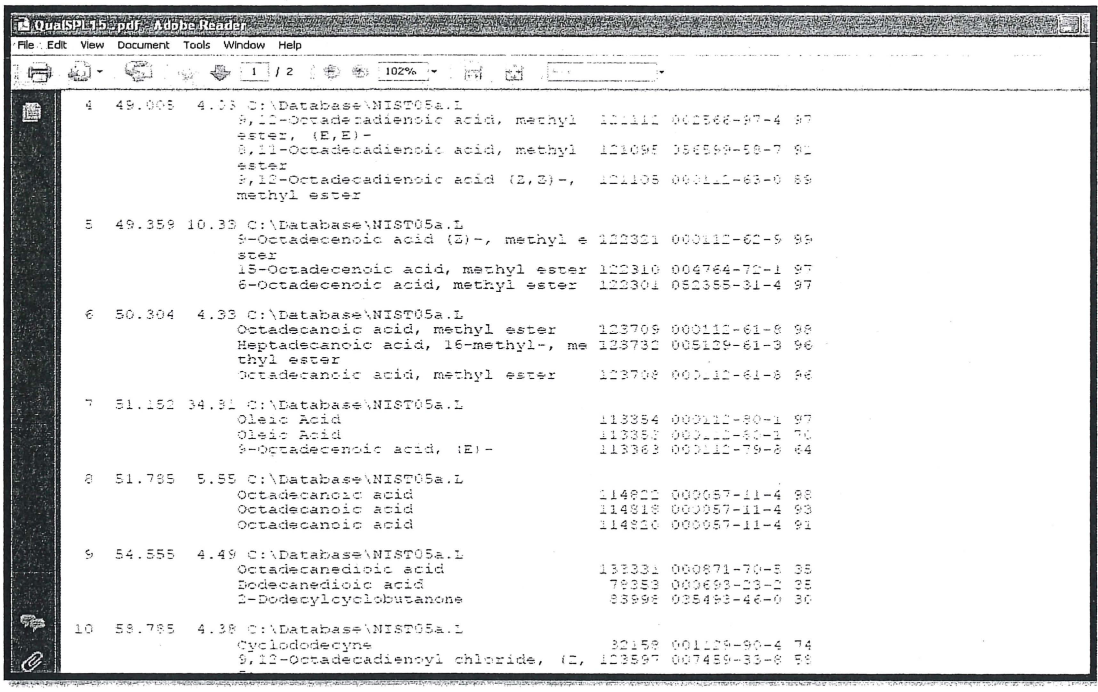
APPENDIX A16 (PRODUCT 15)





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                     ester, (E,E)-
                     8,11-Octadecadienoic acid, methyl  121095 056599-58-7 91
                     ester
                     9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 89
                     methyl ester

 5   49.359 10.33 C:\Database\NIST05a.L
                     9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                     ster
                     15-Octadecenoic acid, methyl ester 122310 004764-72-1 97
                     6-Octadecenoic acid, methyl ester  122301 052355-31-4 97

 6   50.304   4.33 C:\Database\NIST05a.L
                     Octadecanoic acid, methyl ester    123709 000112-61-8 98
                     Heptadecanoic acid, 16-methyl-, me 123732 005129-61-3 96
                     thyl ester
                     Octadecanoic acid, methyl ester    123708 000112-61-8 96

 7   51.152 34.31 C:\Database\NIST05a.L
                     Oleic Acid                         113354 000112-80-1 97
                     Oleic Acid                         113352 000112-80-1 70
                     9-Octadecenoic acid, (E)-          113363 000112-79-8 64

 8   51.785   5.55 C:\Database\NIST05a.L
                     Octadecanoic acid                  114822 000057-11-4 98
                     Octadecanoic acid                  114818 000057-11-4 93
                     Octadecanoic acid                  114820 000057-11-4 91

 9   54.555   4.49 C:\Database\NIST05a.L
                     Octadecanedioic acid               133331 000871-70-5 35
                     Dodecanedioic acid                  79353 000693-23-2 35
                     2-Dodecylcyclobutanone              83998 035493-46-0 30

10   58.785   4.38 C:\Database\NIST05a.L
                     Cyclododecyne                       32158 001129-90-4 74
                     9,12-Octadecadienoyl chloride, (Z, 123597 007459-33-8 58
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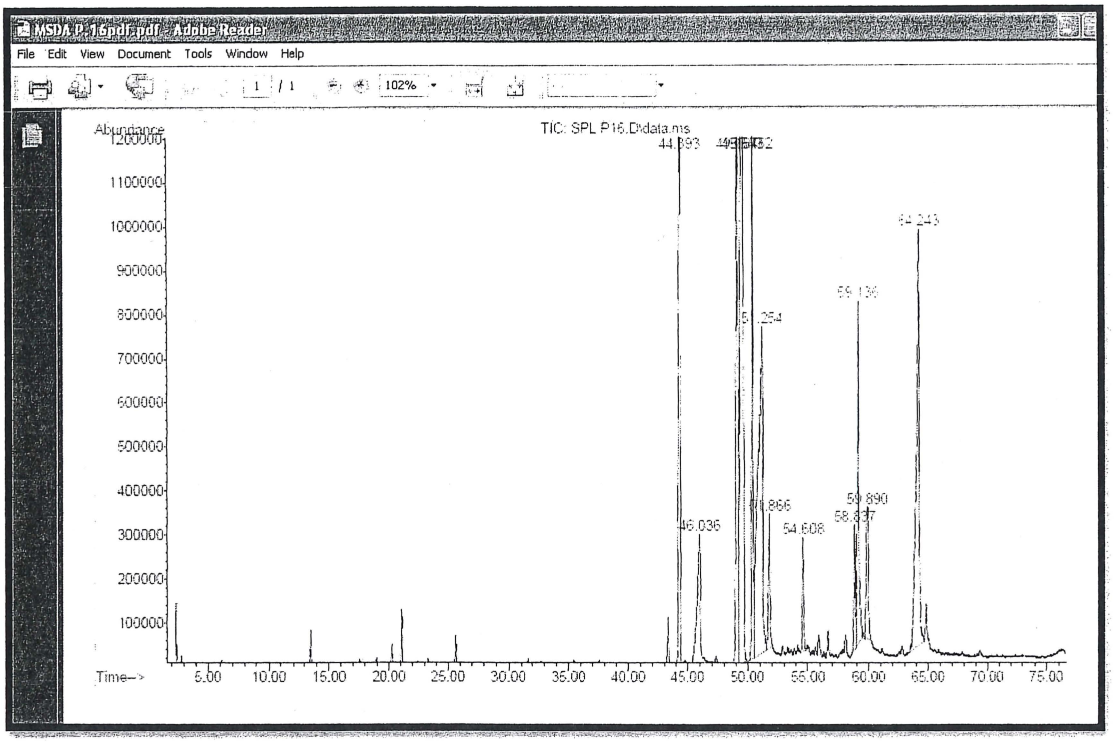
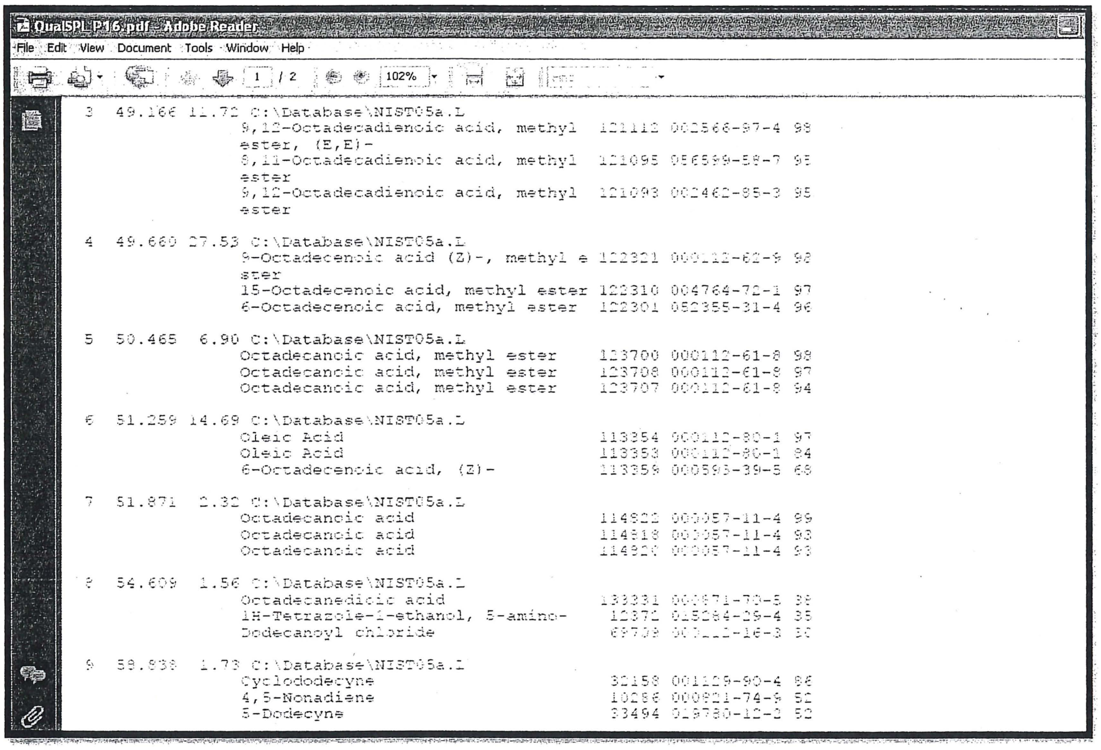
APPENDIX A17 (PRODUCT 16)





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                 ester, (E,E)-
                 8,11-Octadecadienoic acid, methyl  121095 056599-58-7 95
                 ester
                 9,12-Octadecadienoic acid, methyl  121093 002462-85-3 95
                 ester

 4  49.660 27.53 C:\Database\NIST05a.L
                 9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 98
                 ster
                 15-Octadecenoic acid, methyl ester 122310 004764-72-1 97
                 6-Octadecenoic acid, methyl ester  122301 052355-31-4 96

 5  50.465  6.90 C:\Database\NIST05a.L
                 Octadecanoic acid, methyl ester    123700 000112-61-8 98
                 Octadecanoic acid, methyl ester    123708 000112-61-8 97
                 Octadecanoic acid, methyl ester    123707 000112-61-8 94

 6  51.259 14.69 C:\Database\NIST05a.L
                 Oleic Acid                         113354 000112-80-1 97
                 Oleic Acid                         113353 000112-80-1 84
                 6-Octadecenoic acid, (Z)-          113359 000593-39-5 68

 7  51.871  2.32 C:\Database\NIST05a.L
                 Octadecanoic acid                  114822 000057-11-4 99
                 Octadecanoic acid                  114818 000057-11-4 93
                 Octadecanoic acid                  114820 000057-11-4 93

 8  54.609  1.56 C:\Database\NIST05a.L
                 Octadecanedioic acid               133331 000871-70-5 38
                 1H-Tetrazole-1-ethanol, 5-amino-    12372 015284-29-4 35
                 Dodecanoyl chloride                 69709 000112-16-3 30

 9  58.838  1.73 C:\Database\NIST05a.L
                 Cyclododecyne                       32158 001129-90-4 86
                 4,5-Nonadiene                       10286 000821-74-9 52
                 5-Dodecyne                          33494 019780-12-2 52
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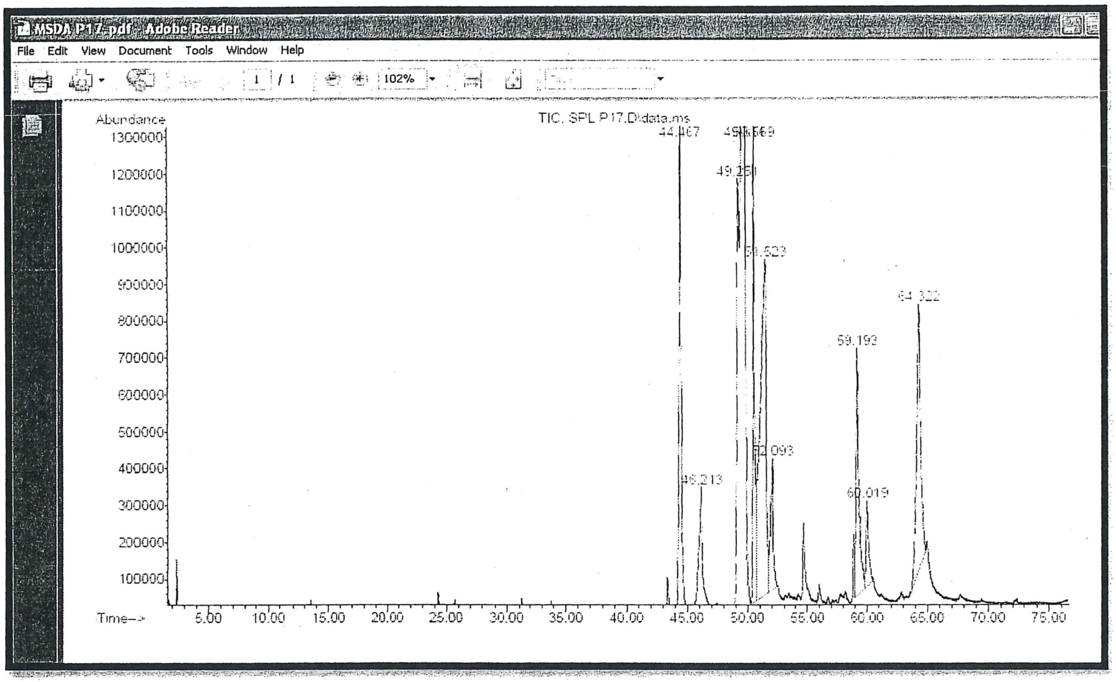
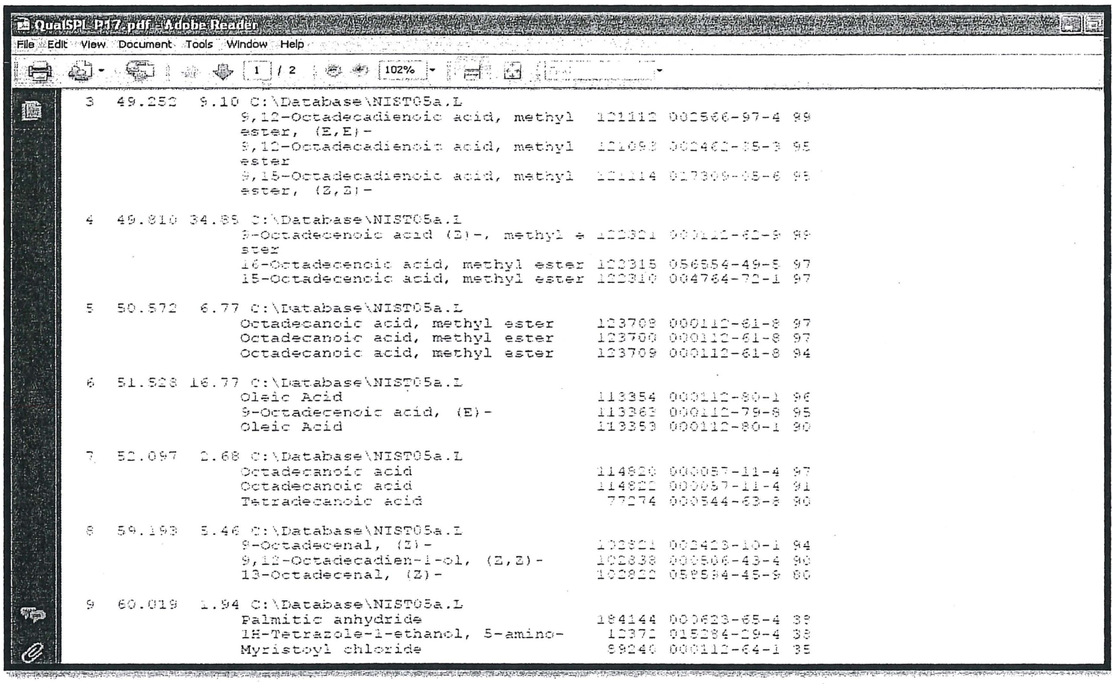
APPENDIX A18 (PRODUCT 17)





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                  ester, (E,E)-
                  9,12-Octadecadienoic acid, methyl  121093 002462-85-3 95
                  ester
                  9,15-Octadecadienoic acid, methyl  121114 017309-05-6 95
                  ester, (Z,Z)-

4   49.810 34.85 C:\Database\NIST05a.L
                  9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                  ster
                  16-Octadecenoic acid, methyl ester 122315 056554-49-5 97
                  15-Octadecenoic acid, methyl ester 122310 004764-72-1 97

5   50.572   6.77 C:\Database\NIST05a.L
                  Octadecanoic acid, methyl ester    123708 000112-61-8 97
                  Octadecanoic acid, methyl ester    123700 000112-61-8 97
                  Octadecanoic acid, methyl ester    123709 000112-61-8 94

6   51.528 16.77 C:\Database\NIST05a.L
                  Oleic Acid                         113354 000112-80-1 96
                  9-Octadecenoic acid, (E)-          113363 000112-79-8 95
                  Oleic Acid                         113353 000112-80-1 90

7   52.097   2.68 C:\Database\NIST05a.L
                  Octadecanoic acid                  114820 000057-11-4 97
                  Octadecanoic acid                  114822 000057-11-4 91
                  Tetradecanoic acid                  77274 000544-63-8 90

8   59.193   5.46 C:\Database\NIST05a.L
                  9-Octadecenal, (Z)-                102821 002423-10-1 94
                  9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 90
                  13-Octadecenal, (Z)-               102822 058594-45-9 80

9   60.019   1.94 C:\Database\NIST05a.L
                  Palmitic anhydride                 184144 000623-65-4 38
                  1H-Tetrazole-1-ethanol, 5-amino-    12372 015284-29-4 38
                  Myristoyl chloride                  89240 000112-64-1 35
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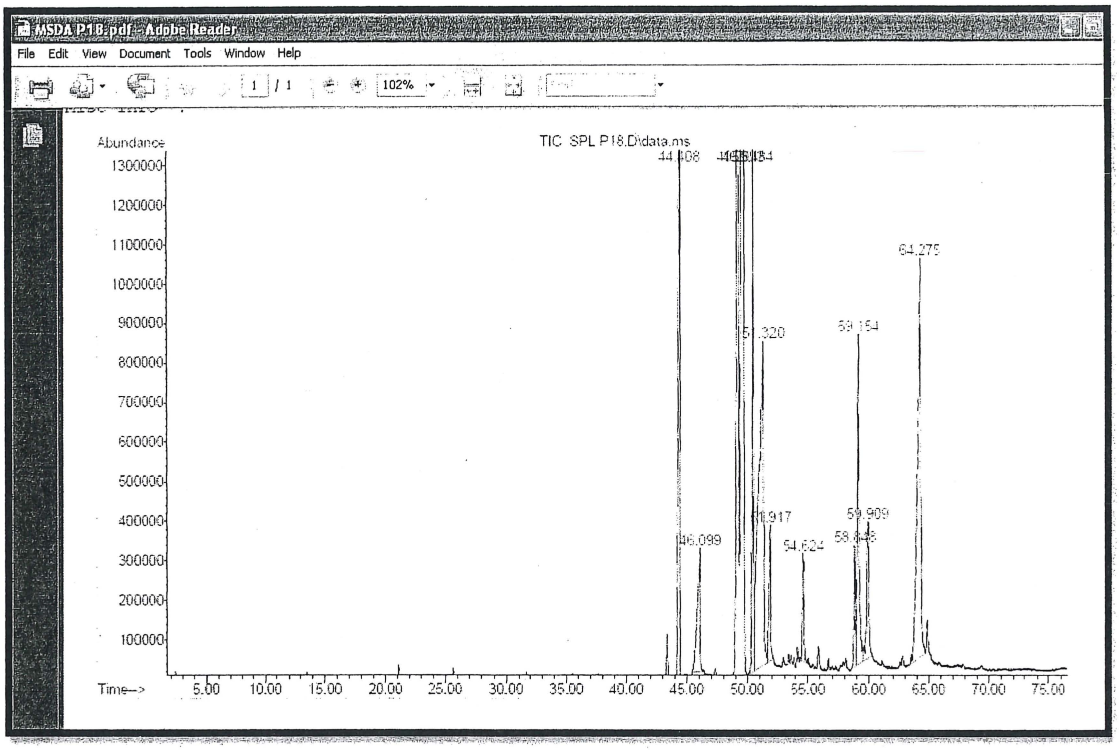
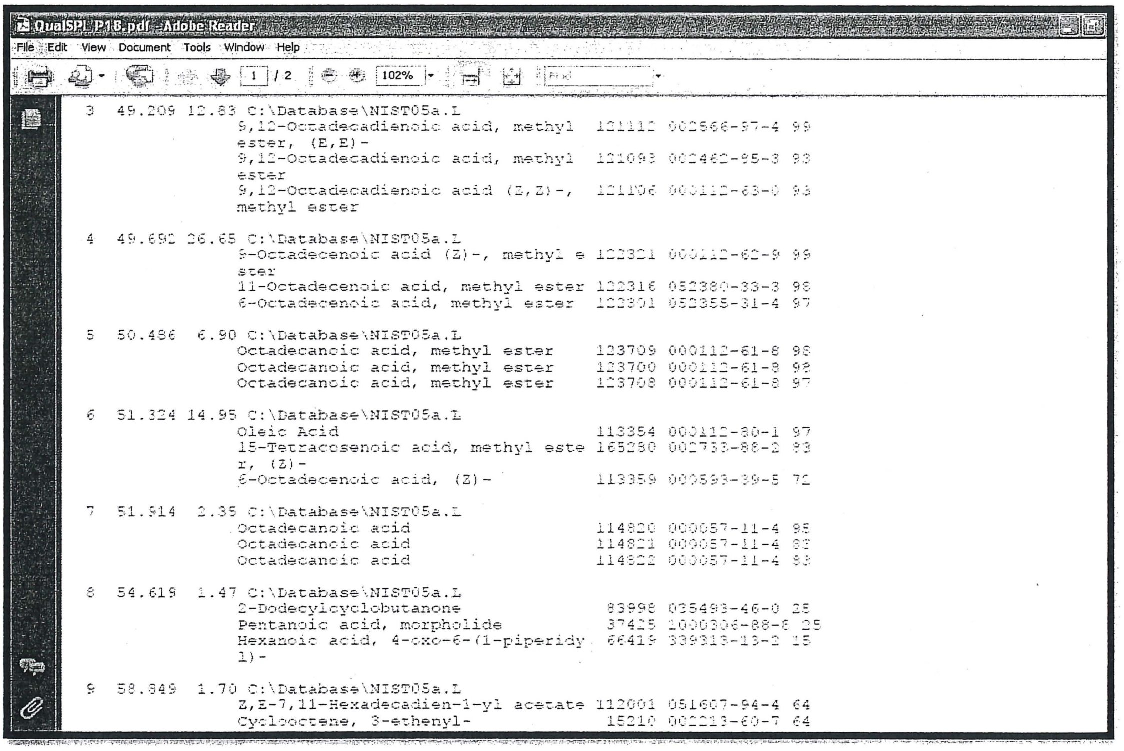
APPENDIX A19 (PRODUCT 18)





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  3  49.209 12.83 C:\Database\NIST05a.L
                  9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
                  ester, (E,E)-
                  9,12-Octadecadienoic acid, methyl  121093 002462-95-3 93
                  ester
                  9,12-Octadecadienoic acid (Z,Z)-,  121106 000112-63-0 93
                  methyl ester

  4  49.692 26.65 C:\Database\NIST05a.L
                  9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                  ster
                  11-Octadecenoic acid, methyl ester 122316 052380-33-3 98
                  6-Octadecenoic acid, methyl ester  122301 052355-31-4 97

  5  50.486  6.90 C:\Database\NIST05a.L
                  Octadecanoic acid, methyl ester    123709 000112-61-8 98
                  Octadecanoic acid, methyl ester    123700 000112-61-8 98
                  Octadecanoic acid, methyl ester    123708 000112-61-8 97

  6  51.324 14.95 C:\Database\NIST05a.L
                  Oleic Acid                         113354 000112-80-1 97
                  15-Tetracosenoic acid, methyl este 165280 002733-88-2 93
                  r, (Z)-
                  6-Octadecenoic acid, (Z)-          113359 000593-39-5 72

  7  51.914  2.35 C:\Database\NIST05a.L
                  Octadecanoic acid                  114820 000057-11-4 95
                  Octadecanoic acid                  114821 000057-11-4 87
                  Octadecanoic acid                  114822 000057-11-4 83

  8  54.619  1.47 C:\Database\NIST05a.L
                  2-Dodecylcyclobutanone              83998 035493-46-0 25
                  Pentanoic acid, morpholide          37425 1000306-88-8 25
                  Hexanoic acid, 4-oxo-6-(1-piperidy  66419 339313-13-2 15
                  l)-

  9  58.849  1.70 C:\Database\NIST05a.L
                  Z,E-7,11-Hexadecadien-1-yl acetate 112001 051607-94-4 64
                  Cyclooctene, 3-ethenyl-             15210 002213-60-7 64
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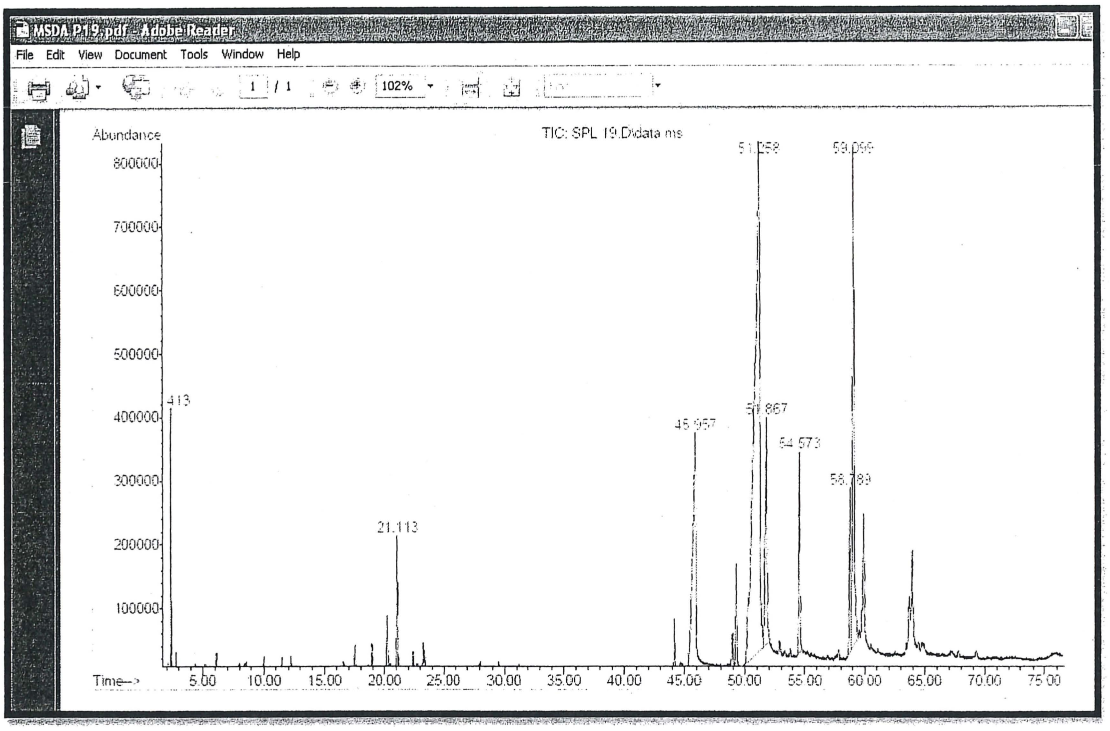
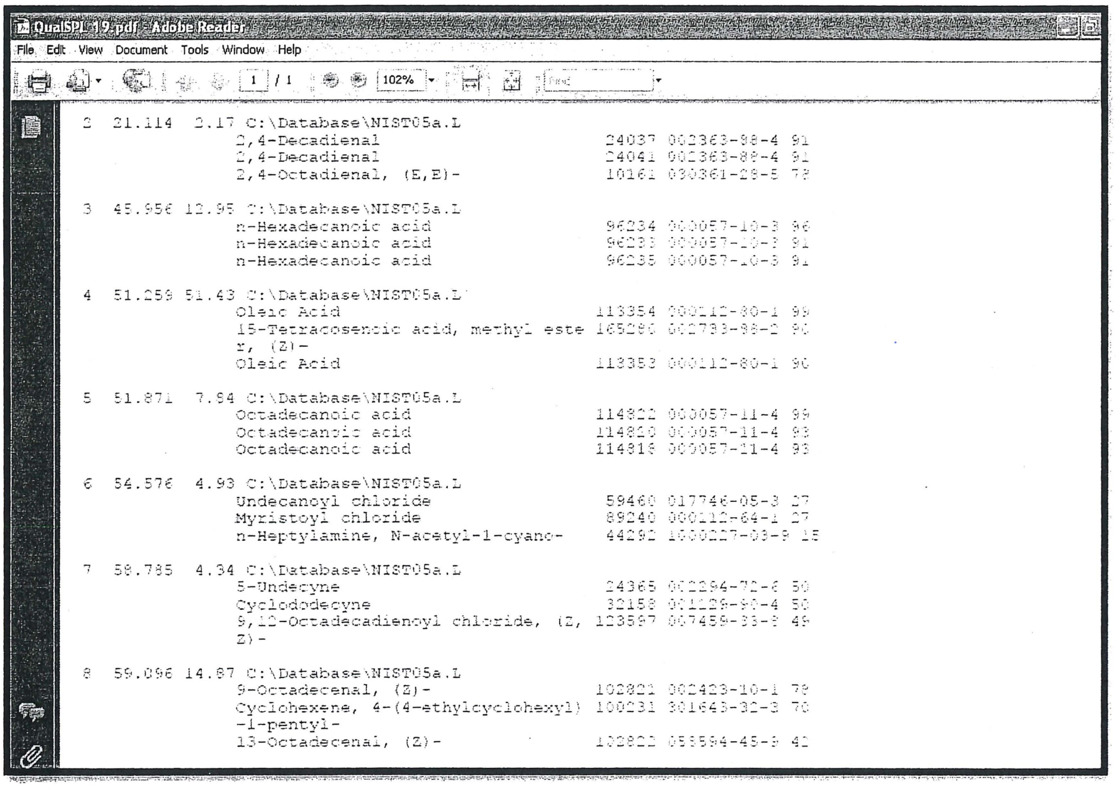
APPENDIX A20 (PRODUCT 19)





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2  21.114   2.17 C:\Database\NIST05a.L
                2,4-Decadienal                        24037 002363-88-4 91
                2,4-Decadienal                        24041 002363-88-4 91
                2,4-Octadienal, (E,E)-                10161 030361-28-5 78

3  45.956 12.95 C:\Database\NIST05a.L
                n-Hexadecanoic acid                   96234 000057-10-3 96
                n-Hexadecanoic acid                   96233 000057-10-3 91
                n-Hexadecanoic acid                   96235 000057-10-3 91

4  51.259 51.43 C:\Database\NIST05a.L
                Oleic Acid                           113354 000112-80-1 99
                15-Tetracosenoic acid, methyl este 165280 002733-88-2 90
                r, (Z)-
                Oleic Acid                           113353 000112-80-1 90

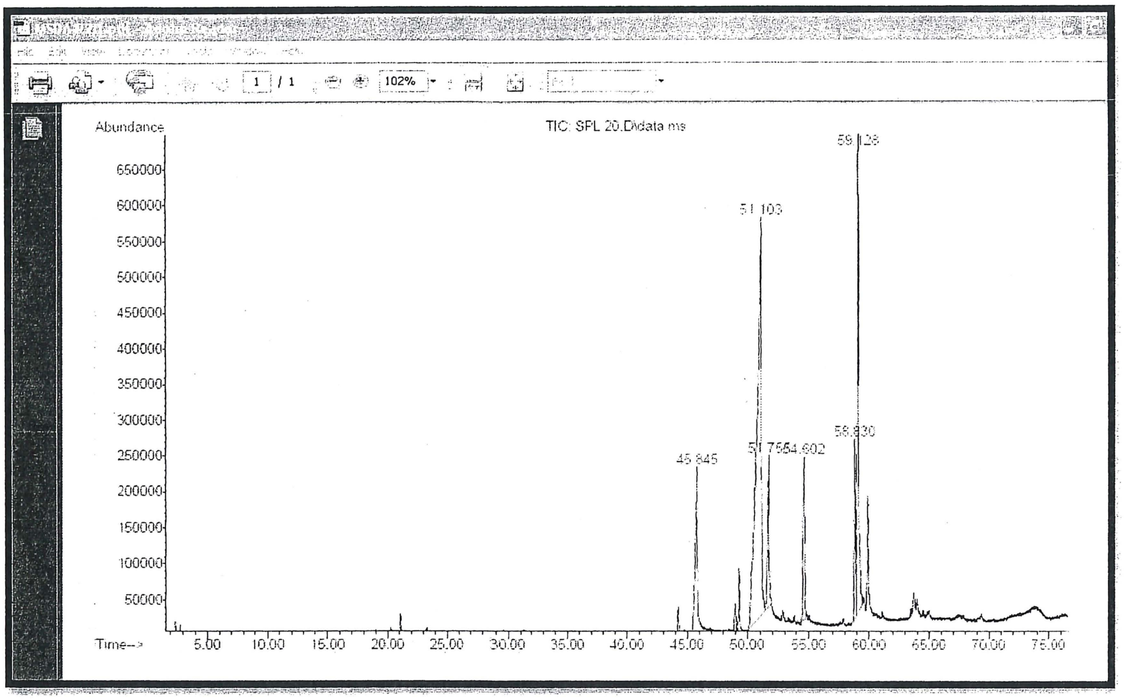
5  51.871   7.84 C:\Database\NIST05a.L
                Octadecanoic acid                    114822 000057-11-4 99
                Octadecanoic acid                    114810 000057-11-4 93
                Octadecanoic acid                    114816 000057-11-4 93

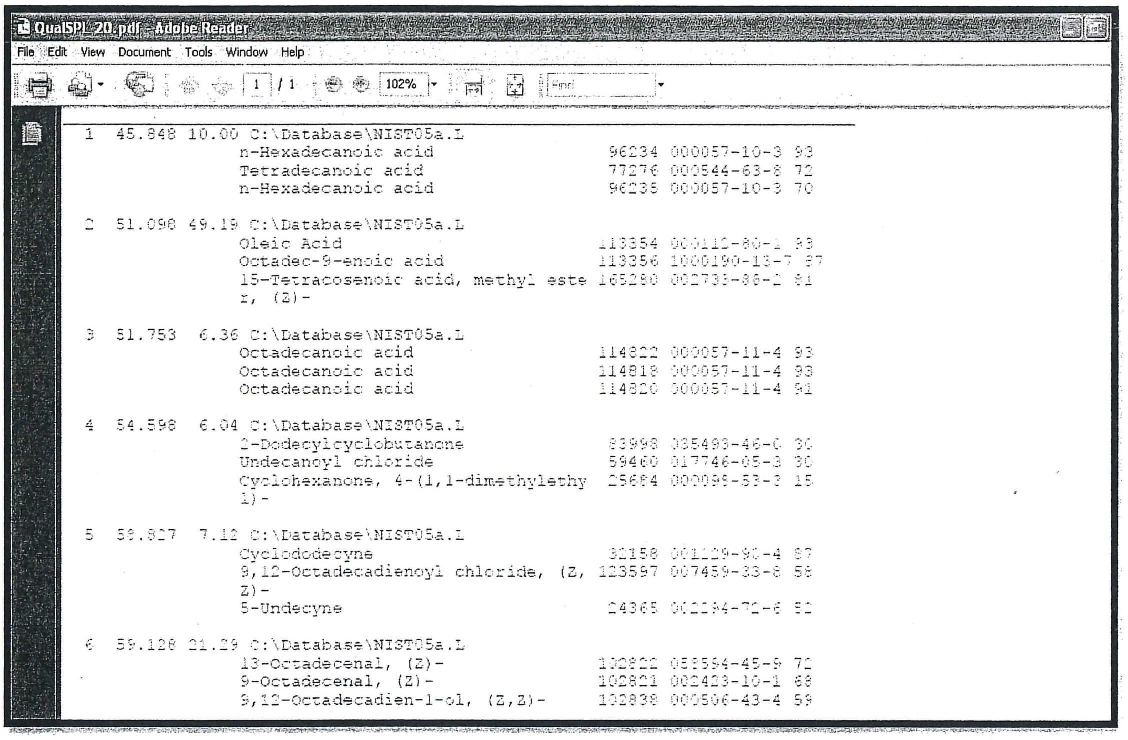
6  54.576   4.93 C:\Database\NIST05a.L
                Undecanoyl chloride                   59460 017746-05-3 27
                Myristoyl chloride                    89240 000112-64-1 27
                n-Heptylamine, N-acetyl-1-cyano-      44292 1000227-03-9 15

7  58.785   4.34 C:\Database\NIST05a.L
                5-Undecyne                            24365 002294-72-6 50
                Cyclododecyne                         32158 001129-90-4 50
                9,12-Octadecadienoyl chloride, (Z, 123597 007459-33-8 49
                Z)-

8  59.096 14.87 C:\Database\NIST05a.L
                9-Octadecenal, (Z)-                  102821 002423-10-1 78
                Cyclohexene, 4-(4-ethylcyclohexyl) 100231 301643-32-3 70
                -1-pentyl-
                13-Octadecenal, (Z)-                 102822 058594-45-9 42
```

APPENDIX A 21(PRODUCT 20)





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1  45.848 10.00 C:\Database\NIST05a.L
               n-Hexadecanoic acid                   96234 000057-10-3 93
               Tetradecanoic acid                    77276 000544-63-8 72
               n-Hexadecanoic acid                   96235 000057-10-3 70

2  51.098 49.19 C:\Database\NIST05a.L
               Oleic Acid                           113354 000112-80-1 93
               Octadec-9-enoic acid                 113356 1000190-13-7 87
               15-Tetracosenoic acid, methyl este 165280 002733-88-2 81
               r, (Z)-

3  51.753  6.36 C:\Database\NIST05a.L
               Octadecanoic acid                    114822 000057-11-4 93
               Octadecanoic acid                    114818 000057-11-4 93
               Octadecanoic acid                    114820 000057-11-4 91

4  54.598  6.04 C:\Database\NIST05a.L
               2-Dodecylcyclobutanone                83998 035493-46-0 30
               Undecanoyl chloride                   59460 017746-05-3 30
               Cyclohexanone, 4-(1,1-dimethylethy  25684 000098-53-3 15
               l)-

5  58.827  7.12 C:\Database\NIST05a.L
               Cyclododecyne                         32158 001129-90-4 87
               9,12-Octadecadienoyl chloride, (Z, 123597 007459-33-8 58
               Z)-
               5-Undecyne                            24365 002294-72-6 52

6  59.128 21.29 C:\Database\NIST05a.L
               13-Octadecenal, (Z)-                 102822 058594-45-9 72
               9-Octadecenal, (Z)-                  102821 002423-10-1 68
               9,12-Octadecadien-1-ol, (Z,Z)-       102838 000506-43-4 59
```
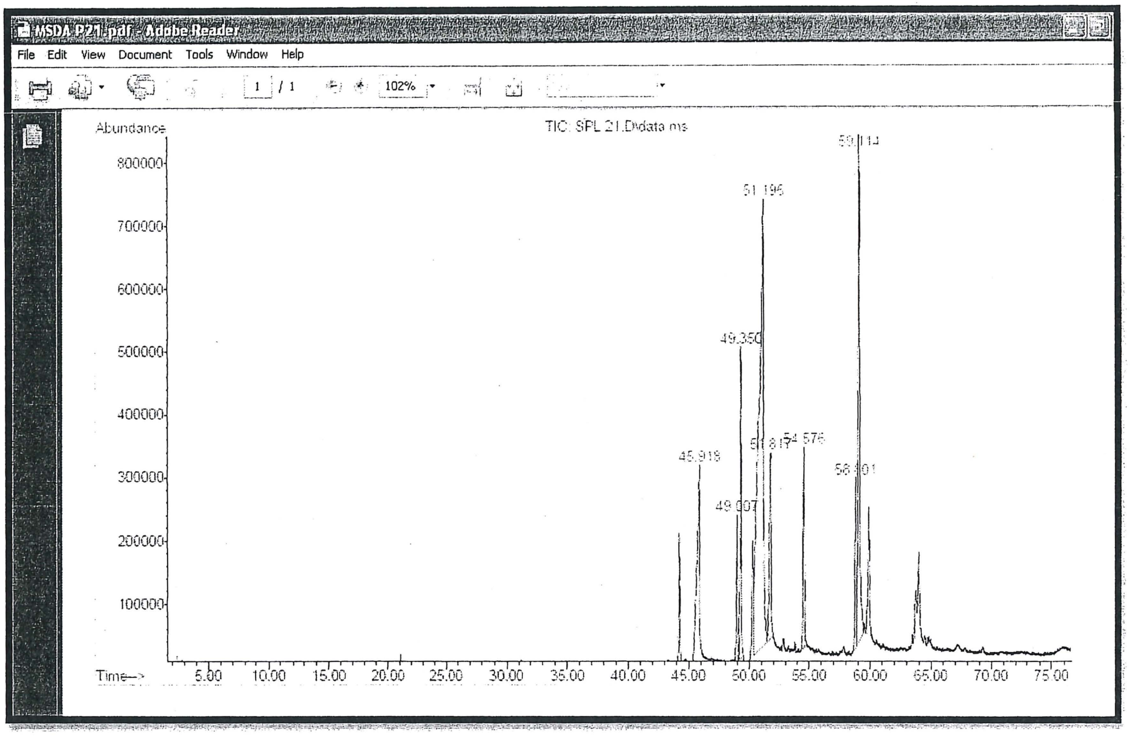
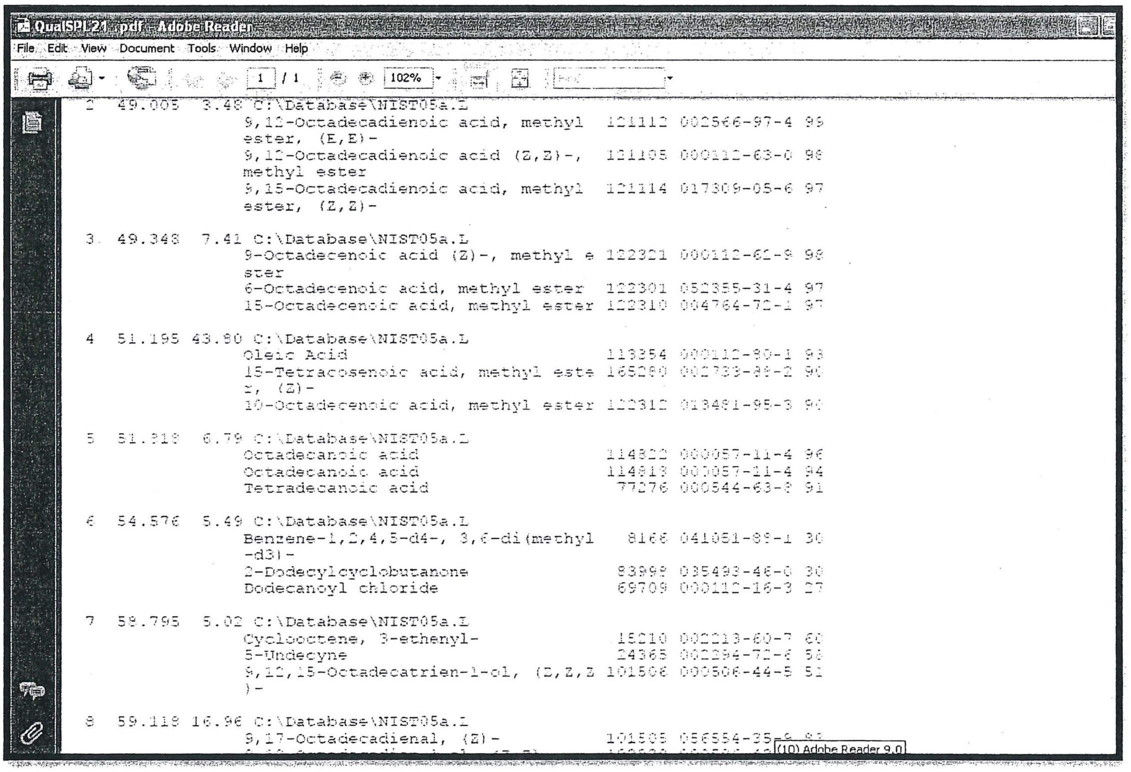

APPENDIX A22 (PRODUCT 21)





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2  49.005  3.48 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
                ester, (E,E)-
                9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 98
                methyl ester
                9,15-Octadecadienoic acid, methyl  121114 017309-05-6 97
                ester, (Z,Z)-

3  49.348  7.41 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 98
                ster
                6-Octadecenoic acid, methyl ester  122301 052355-31-4 97
                15-Octadecenoic acid, methyl ester 122310 004764-72-1 97

4  51.195 43.80 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 93
                15-Tetracosenoic acid, methyl este 165280 002733-88-2 90
                r, (Z)-
                10-Octadecenoic acid, methyl ester 122312 013481-95-3 90

5  51.818  6.79 C:\Database\NIST05a.L
                Octadecanoic acid                  114822 000057-11-4 96
                Octadecanoic acid                  114813 000057-11-4 94
                Tetradecanoic acid                  77276 000544-63-8 91

6  54.576  5.49 C:\Database\NIST05a.L
                Benzene-1,2,4,5-d4-, 3,6-di(methyl   8166 041051-88-1 30
                -d3)-
                2-Dodecylcyclobutanone              83998 035493-46-0 30
                Dodecanoyl chloride                 69709 000112-16-3 27

7  58.795  5.02 C:\Database\NIST05a.L
                Cyclooctene, 3-ethenyl-             15210 002213-60-7 60
                5-Undecyne                          24365 002294-72-6 58
                9,12,15-Octadecatrien-1-ol, (Z,Z,Z 101508 000506-44-5 51
                )-

8  59.118 16.96 C:\Database\NIST05a.L
                9,17-Octadecadienal, (Z)-          101505 056554-35-
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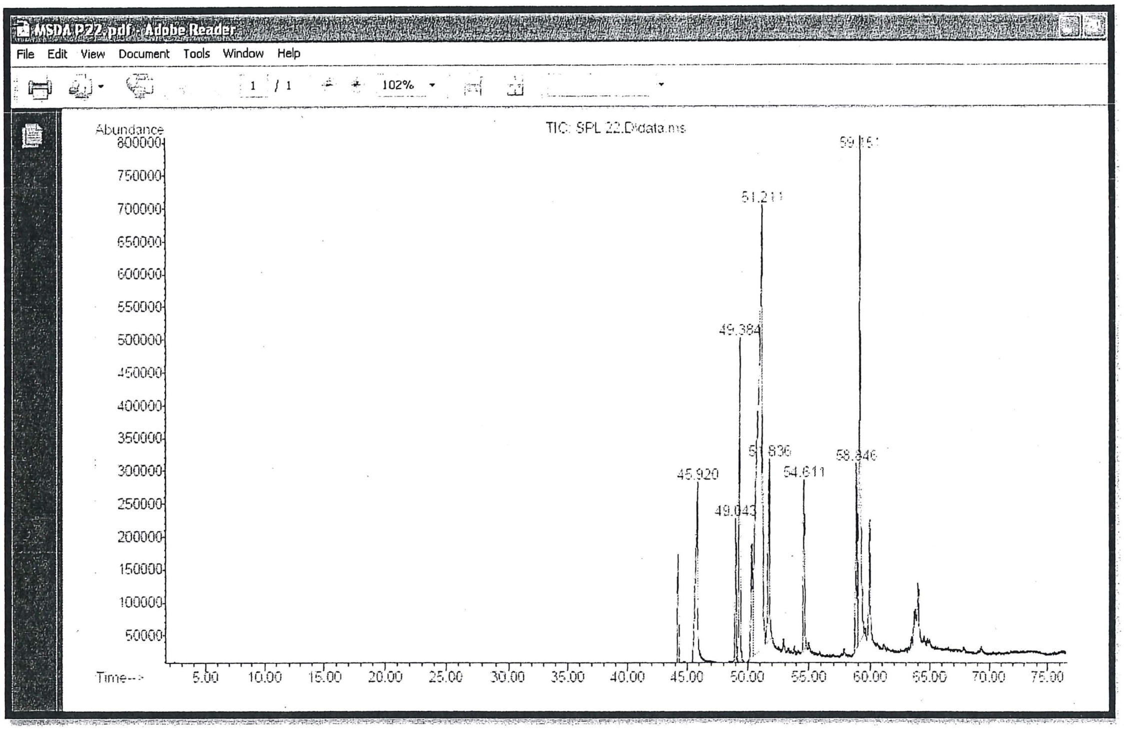
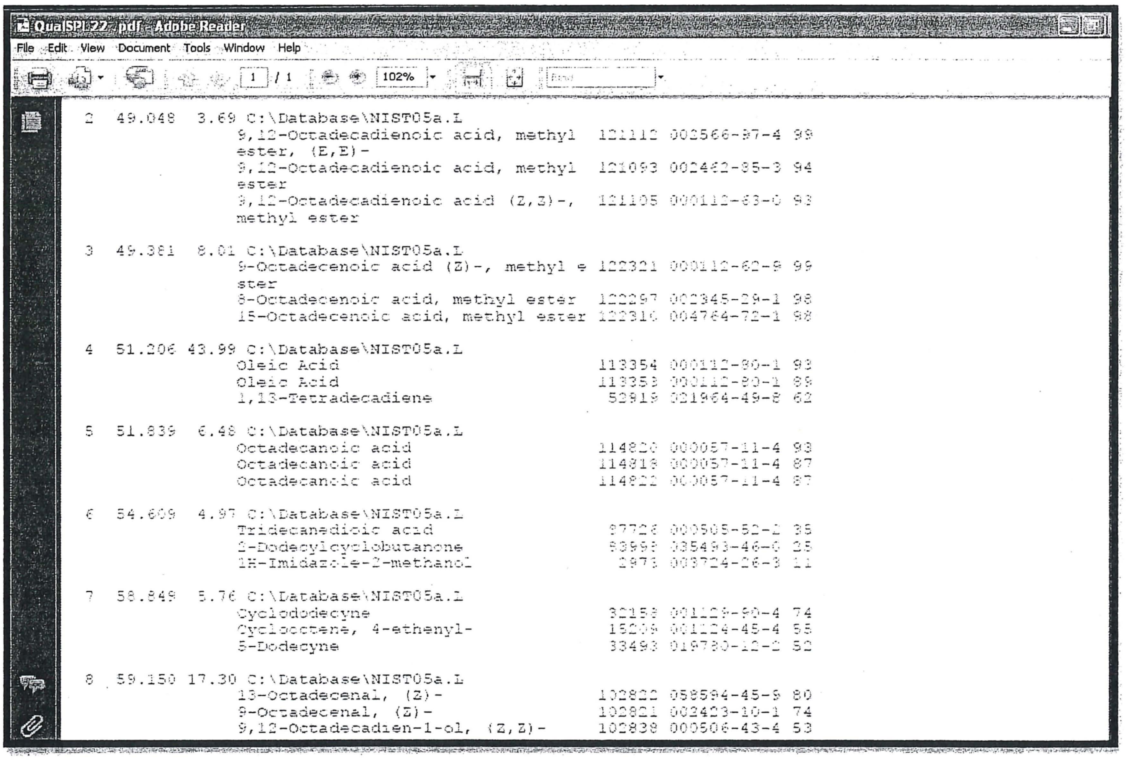
APPENDIX A23 (PRODUCT 22)





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2  49.048  3.69 C:\Database\NIST05a.L
              9,12-Octadecadienoic acid, methyl  121112 002566-97-4 99
              ester, (E,E)-
              9,12-Octadecadienoic acid, methyl  121093 002462-85-3 94
              ester
              9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 93
              methyl ester

3  49.381  8.01 C:\Database\NIST05a.L
              9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
              ster
              8-Octadecenoic acid, methyl ester  122297 002345-29-1 98
              15-Octadecenoic acid, methyl ester 122310 004764-72-1 98

4  51.206 43.99 C:\Database\NIST05a.L
              Oleic Acid                         113354 000112-80-1 93
              Oleic Acid                         113353 000112-80-1 89
              1,13-Tetradecadiene                 52919 021964-49-8 62

5  51.839  6.48 C:\Database\NIST05a.L
              Octadecanoic acid                  114820 000057-11-4 93
              Octadecanoic acid                  114818 000057-11-4 87
              Octadecanoic acid                  114822 000057-11-4 87

6  54.609  4.97 C:\Database\NIST05a.L
              Tridecanedioic acid                 97728 000505-52-2 35
              2-Dodecylcyclobutanone              83998 035493-46-0 25
              1H-Imidazole-2-methanol              2973 003724-26-3 11

7  58.849  5.76 C:\Database\NIST05a.L
              Cyclododecyne                       32158 001129-90-4 74
              Cyclooctene, 4-ethenyl-             15209 001124-45-4 55
              5-Dodecyne                          33493 019780-12-2 52

8  59.150 17.30 C:\Database\NIST05a.L
              13-Octadecenal, (Z)-               102822 058594-45-9 80
              9-Octadecenal, (Z)-                102821 002423-10-1 74
              9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 53
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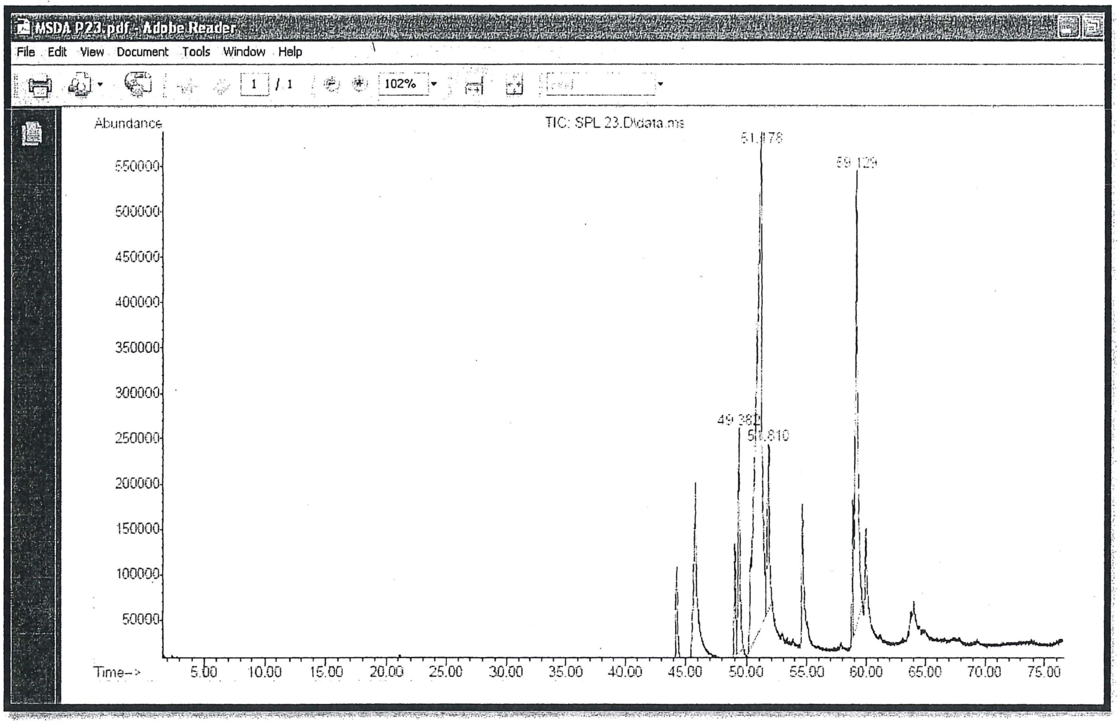
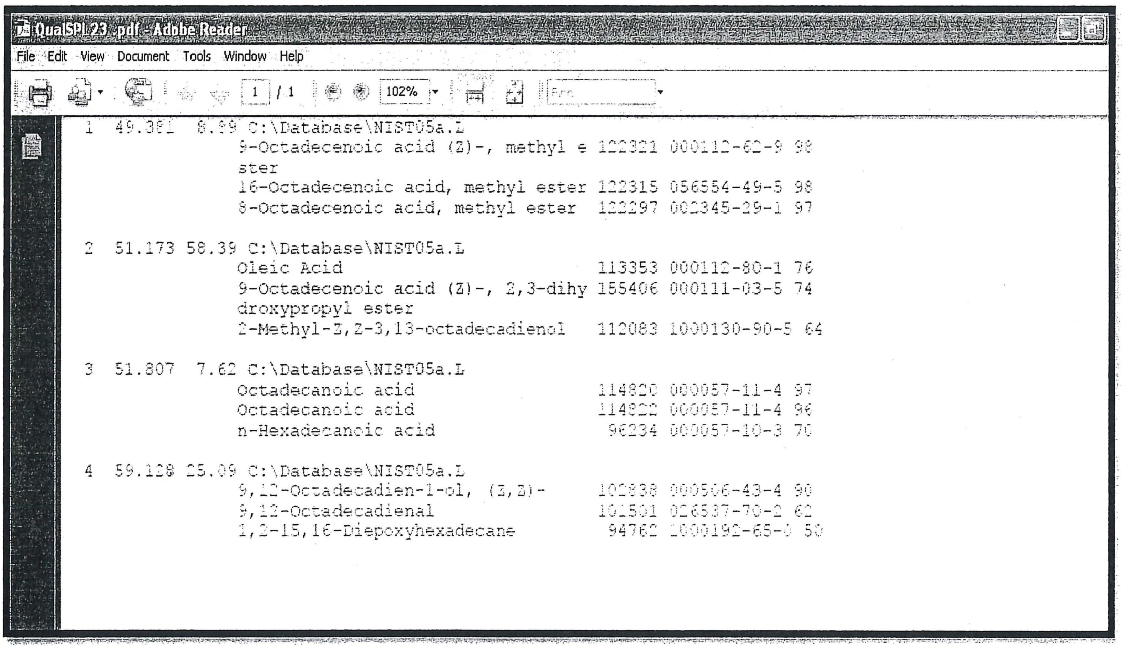
APPENDIX A24 (PRODUCT 23)





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1  49.381  8.99 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 98
                ster
                16-Octadecenoic acid, methyl ester 122315 056554-49-5 98
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 97

2  51.173 58.39 C:\Database\NIST05a.L
                Oleic Acid                         113353 000112-80-1 76
                9-Octadecenoic acid (Z)-, 2,3-dihy 155406 000111-03-5 74
                droxypropyl ester
                2-Methyl-Z,Z-3,13-octadecadienol   112083 1000130-90-5 64

3  51.807  7.62 C:\Database\NIST05a.L
                Octadecanoic acid                  114820 000057-11-4 97
                Octadecanoic acid                  114822 000057-11-4 96
                n-Hexadecanoic acid                 96234 000057-10-3 70

4  59.128 25.09 C:\Database\NIST05a.L
                9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 90
                9,12-Octadecadienal                101501 026537-70-2 62
                1,2-15,16-Diepoxyhexadecane         94762 1000192-65-0 50
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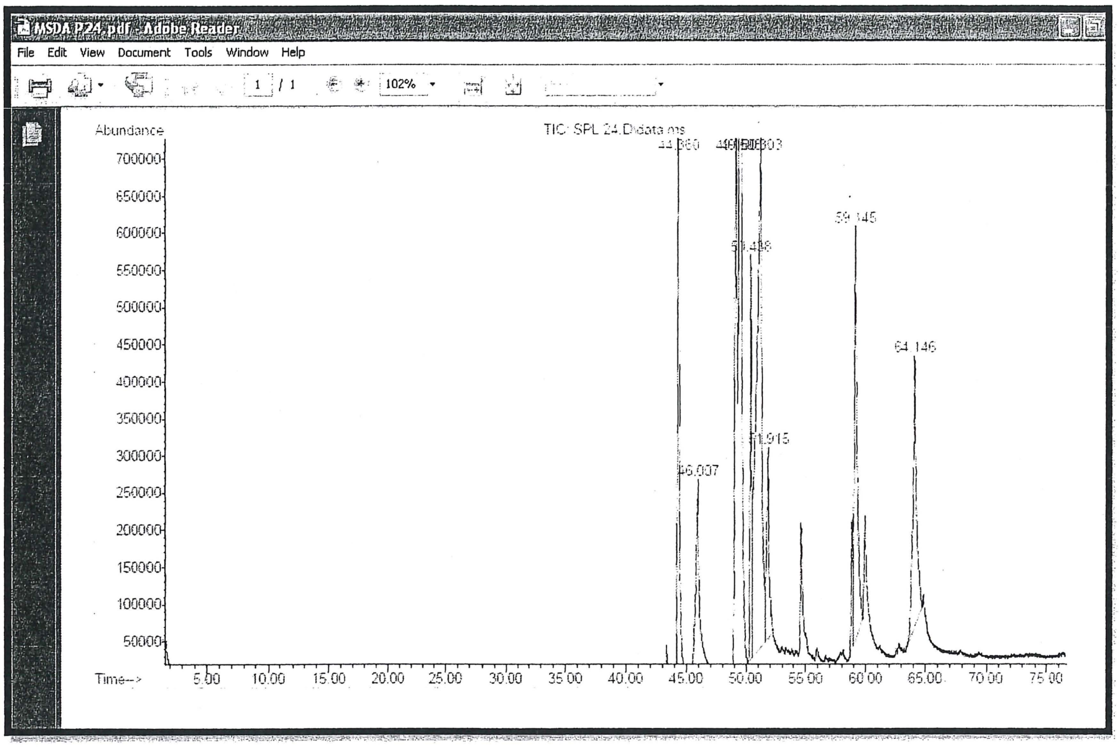
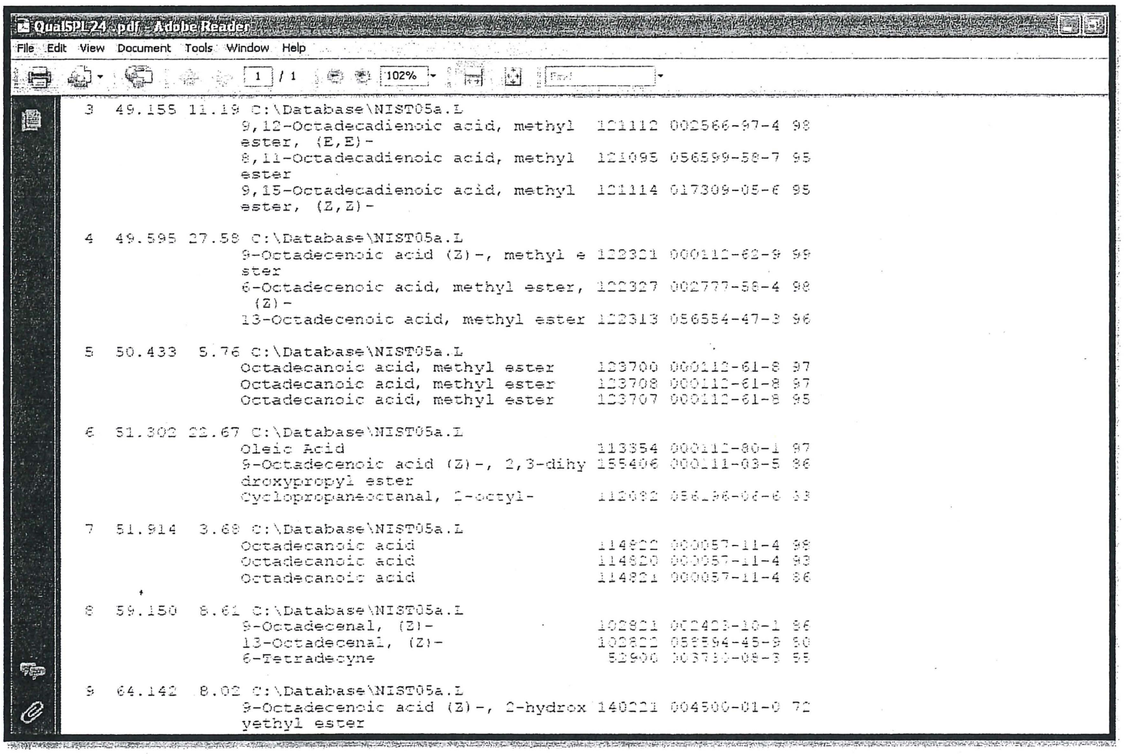
APPENDIX A 25 (PRODUCT 24)





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3  49.155 11.19 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 98
                ester, (E,E)-
                8,11-Octadecadienoic acid, methyl  121095 056599-58-7 95
                ester
                9,15-Octadecadienoic acid, methyl  121114 017309-05-6 95
                ester, (Z,Z)-

4  49.595 27.58 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                ster
                6-Octadecenoic acid, methyl ester, 122327 002777-58-4 98
                 (Z)-
                13-Octadecenoic acid, methyl ester 122313 056554-47-3 96

5  50.433  5.76 C:\Database\NIST05a.L
                Octadecanoic acid, methyl ester    123700 000112-61-8 97
                Octadecanoic acid, methyl ester    123708 000112-61-8 97
                Octadecanoic acid, methyl ester    123707 000112-61-8 95

6  51.302 22.67 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 97
                9-Octadecenoic acid (Z)-, 2,3-dihy 155406 000111-03-5 86
                droxypropyl ester
                Cyclopropaneoctanal, 2-octyl-      112092 056196-06-6 33

7  51.914  3.68 C:\Database\NIST05a.L
                Octadecanoic acid                  114822 000057-11-4 98
                Octadecanoic acid                  114820 000057-11-4 93
                Octadecanoic acid                  114821 000057-11-4 86

8  59.150  8.61 C:\Database\NIST05a.L
                9-Octadecenal, (Z)-                102821 002423-10-1 86
                13-Octadecenal, (Z)-               102822 058594-45-9 50
                6-Tetradecyne                       52900 003730-08-3 55

9  64.142  8.02 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, 2-hydrox 140221 004500-01-0 72
                yethyl ester
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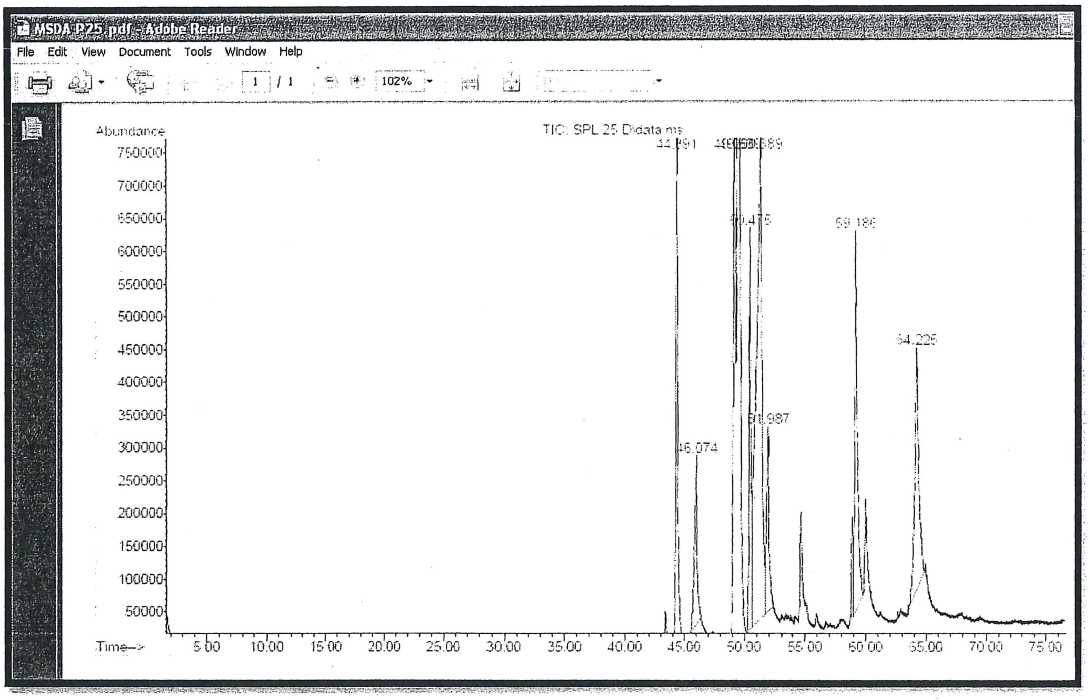
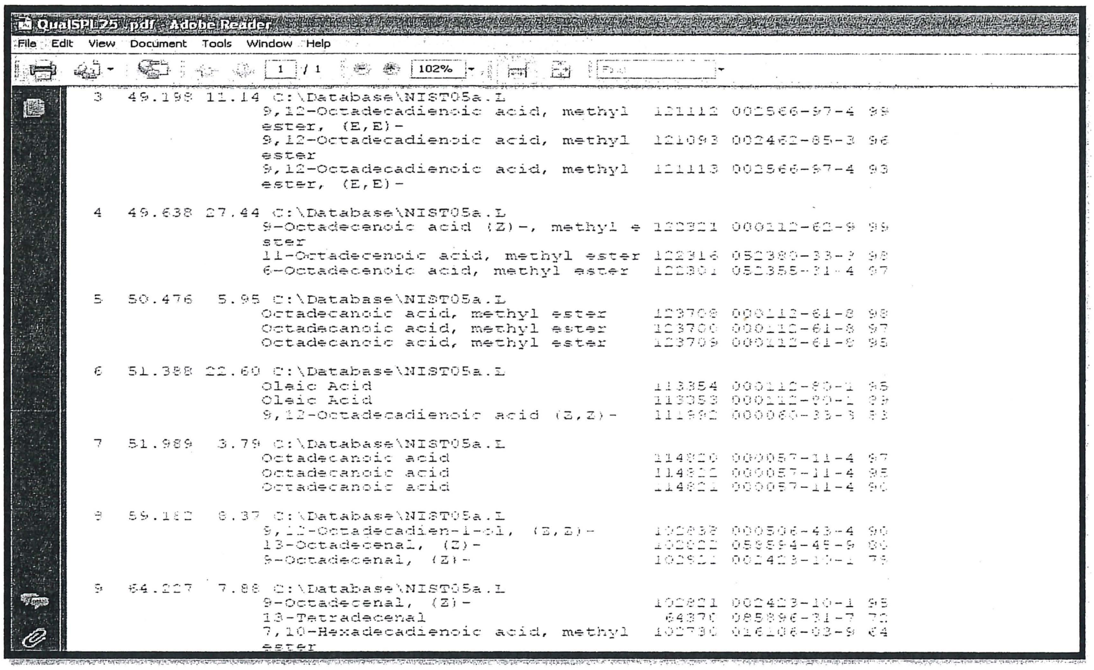
APPENDIX A26 (PRODUCT 25)





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                 ester, (E,E)-
                 9,12-Octadecadienoic acid, methyl  121093 002462-85-3 96
                 ester
                 9,12-Octadecadienoic acid, methyl  121113 002566-97-4 93
                 ester, (E,E)-

4   49.638 27.44 C:\Database\NIST05a.L
                 9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                 ster
                 11-Octadecenoic acid, methyl ester 122316 052380-33-7 98
                 6-Octadecenoic acid, methyl ester  122301 052355-31-4 97

5   50.476  5.95 C:\Database\NIST05a.L
                 Octadecanoic acid, methyl ester    123708 000112-61-8 98
                 Octadecanoic acid, methyl ester    123700 000112-61-8 97
                 Octadecanoic acid, methyl ester    123709 000112-61-8 95

6   51.388 22.60 C:\Database\NIST05a.L
                 Oleic Acid                         113354 000112-80-1 95
                 Oleic Acid                         113353 000112-80-1 93
                 9,12-Octadecadienoic acid (Z,Z)-   111990 000060-33-3 83

7   51.989  3.79 C:\Database\NIST05a.L
                 Octadecanoic acid                  114820 000057-11-4 97
                 Octadecanoic acid                  114822 000057-11-4 95
                 Octadecanoic acid                  114821 000057-11-4 90

8   59.182  8.37 C:\Database\NIST05a.L
                 9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 90
                 13-Octadecenal, (Z)-               102822 058594-45-9 90
                 9-Octadecenal, (Z)-                102821 002423-10-1 78

9   64.227  7.88 C:\Database\NIST05a.L
                 9-Octadecenal, (Z)-                102821 002423-10-1 95
                 13-Tetradecenal                     64370 085896-31-7 72
                 7,10-Hexadecadienoic acid, methyl  102730 016106-03-9 64
                 ester
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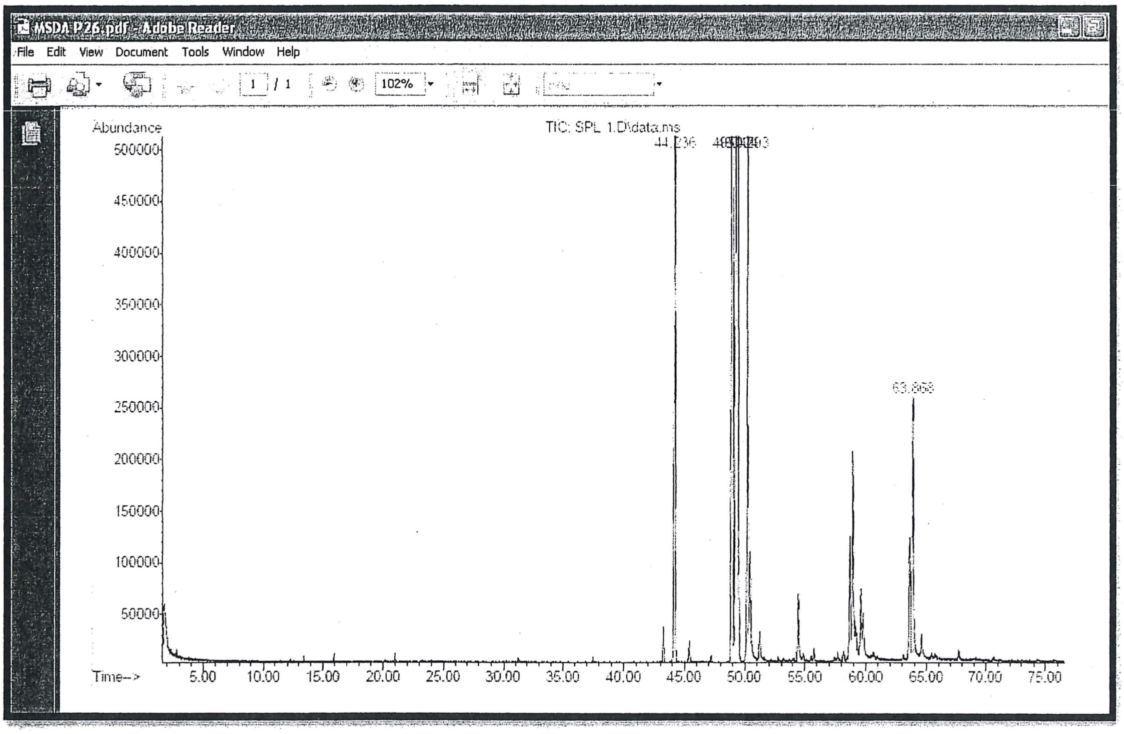
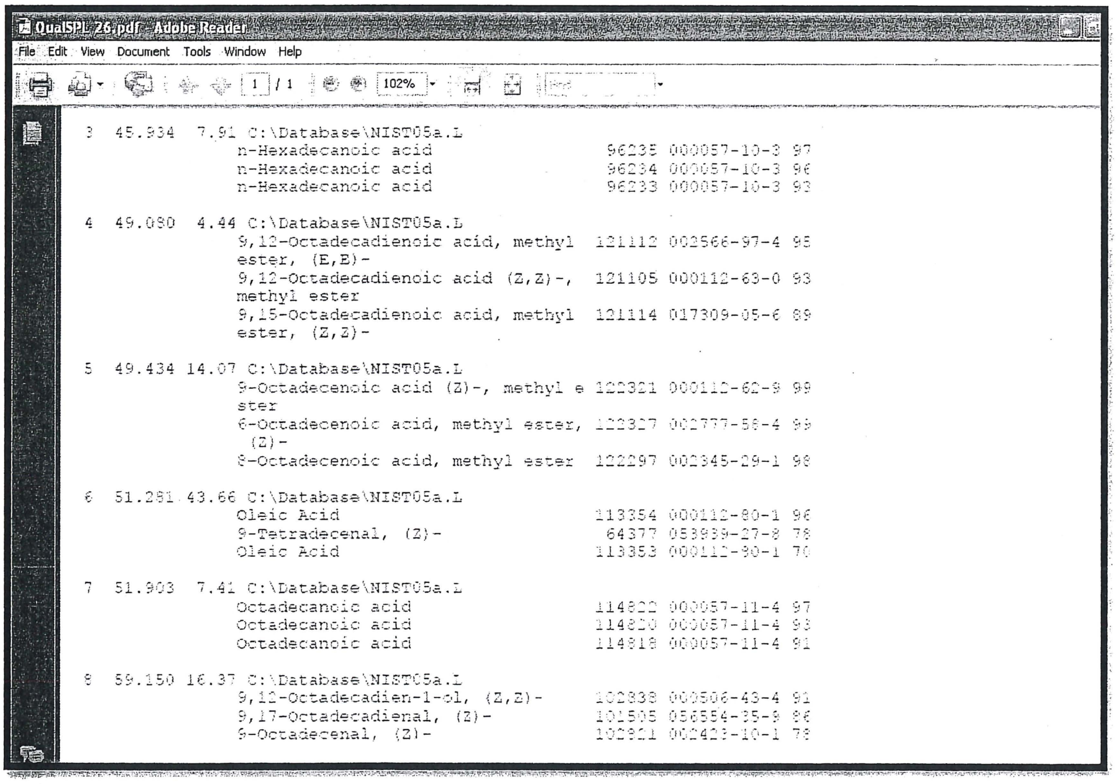
APPENDIX A27 (PRODUCT 26)





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3  45.934  7.91 C:\Database\NIST05a.L
                n-Hexadecanoic acid                   96235 000057-10-3 97
                n-Hexadecanoic acid                   96234 000057-10-3 96
                n-Hexadecanoic acid                   96233 000057-10-3 93

4  49.080  4.44 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 95
                ester, (E,E)-
                9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 93
                methyl ester
                9,15-Octadecadienoic acid, methyl  121114 017309-05-6 89
                ester, (Z,Z)-

5  49.434 14.07 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                ster
                6-Octadecenoic acid, methyl ester, 122327 002777-58-4 99
                 (Z)-
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 98

6  51.281 43.66 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 96
                9-Tetradecenal, (Z)-                64377 053939-27-8 78
                Oleic Acid                         113353 000112-80-1 70

7  51.903  7.41 C:\Database\NIST05a.L
                Octadecanoic acid                  114822 000057-11-4 97
                Octadecanoic acid                  114820 000057-11-4 93
                Octadecanoic acid                  114818 000057-11-4 91

8  59.150 16.37 C:\Database\NIST05a.L
                9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 91
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 86
                9-Octadecenal, (Z)-                102921 002423-10-1 78
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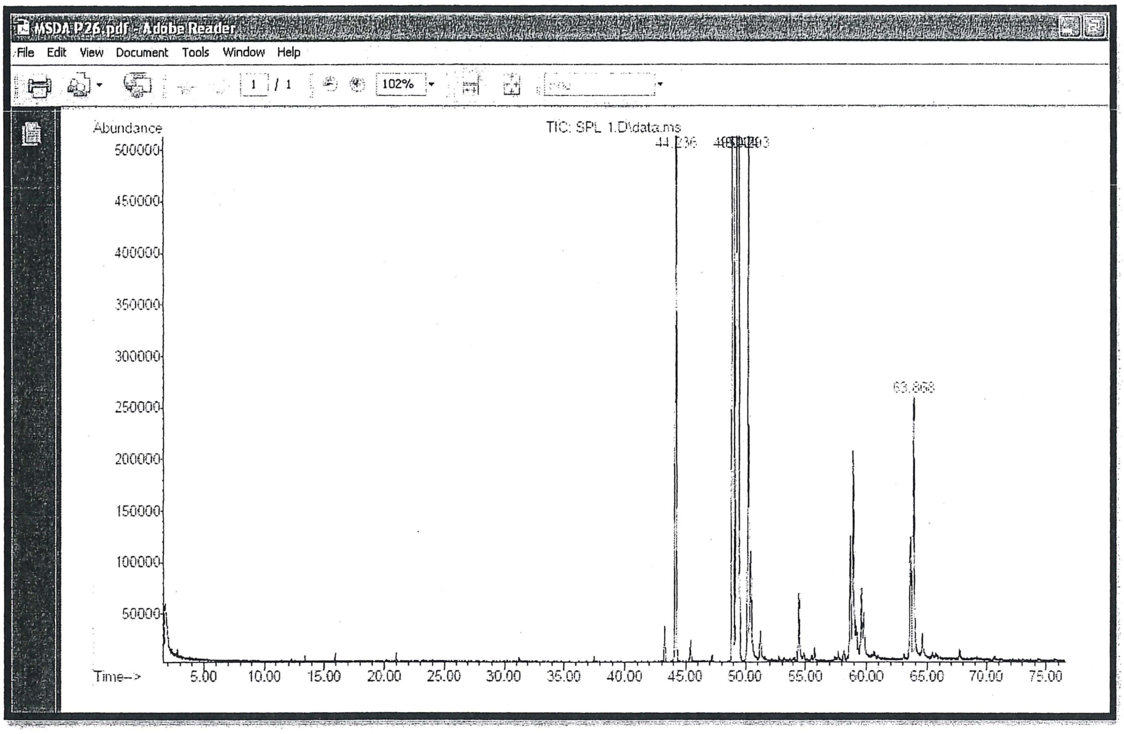
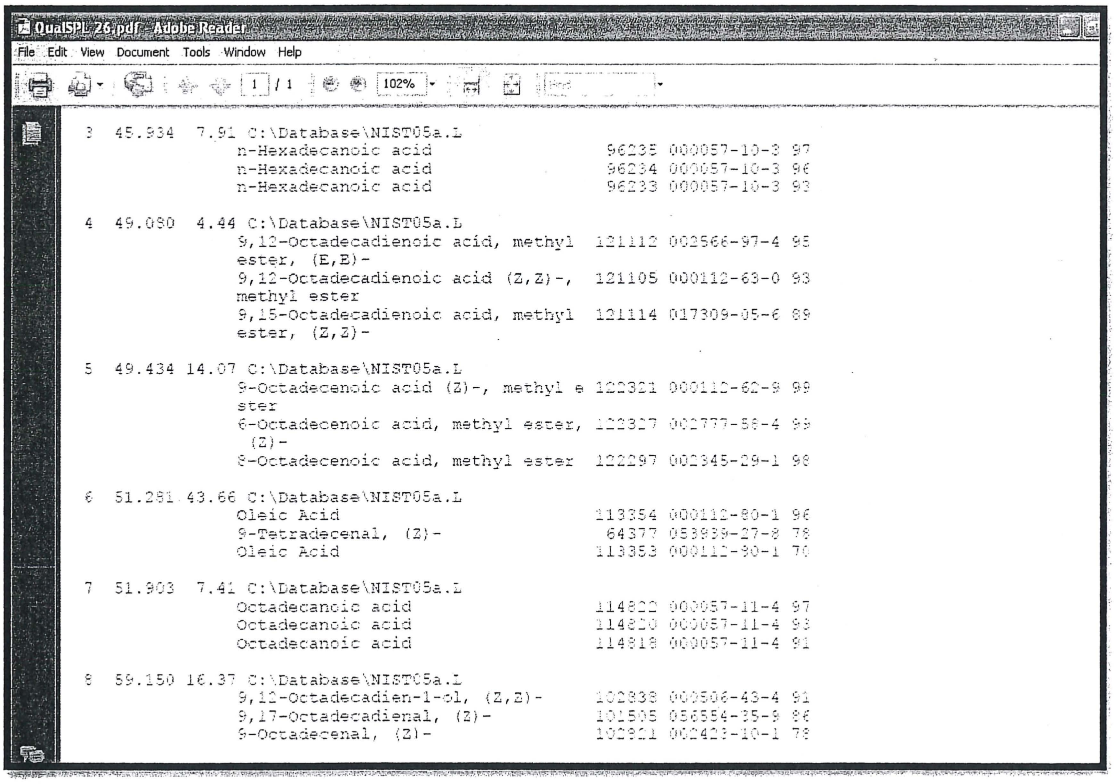
APPENDIX A27 (PRODUCT 26)





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                 n-Hexadecanoic acid                   96235 000057-10-3 97
                 n-Hexadecanoic acid                   96234 000057-10-3 96
                 n-Hexadecanoic acid                   96233 000057-10-3 93

4  49.080  4.44 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid, methyl  121112 002566-97-4 95
                 ester, (E,E)-
                 9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 93
                 methyl ester
                 9,15-Octadecadienoic acid, methyl  121114 017309-05-6 89
                 ester, (Z,Z)-

5  49.434 14.07 C:\Database\NIST05a.L
                 9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                 ster
                 6-Octadecenoic acid, methyl ester, 122327 002777-58-4 99
                  (Z)-
                 8-Octadecenoic acid, methyl ester  122297 002345-29-1 98

6  51.281 43.66 C:\Database\NIST05a.L
                 Oleic Acid                         113354 000112-80-1 96
                 9-Tetradecenal, (Z)-                64377 053939-27-8 78
                 Oleic Acid                         113353 000112-80-1 70

7  51.903  7.41 C:\Database\NIST05a.L
                 Octadecanoic acid                  114822 000057-11-4 97
                 Octadecanoic acid                  114820 000057-11-4 93
                 Octadecanoic acid                  114818 000057-11-4 91

8  59.150 16.37 C:\Database\NIST05a.L
                 9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 91
                 9,17-Octadecadienal, (Z)-          101505 056554-35-9 86
                 9-Octadecenal, (Z)-                102921 002423-10-1 78
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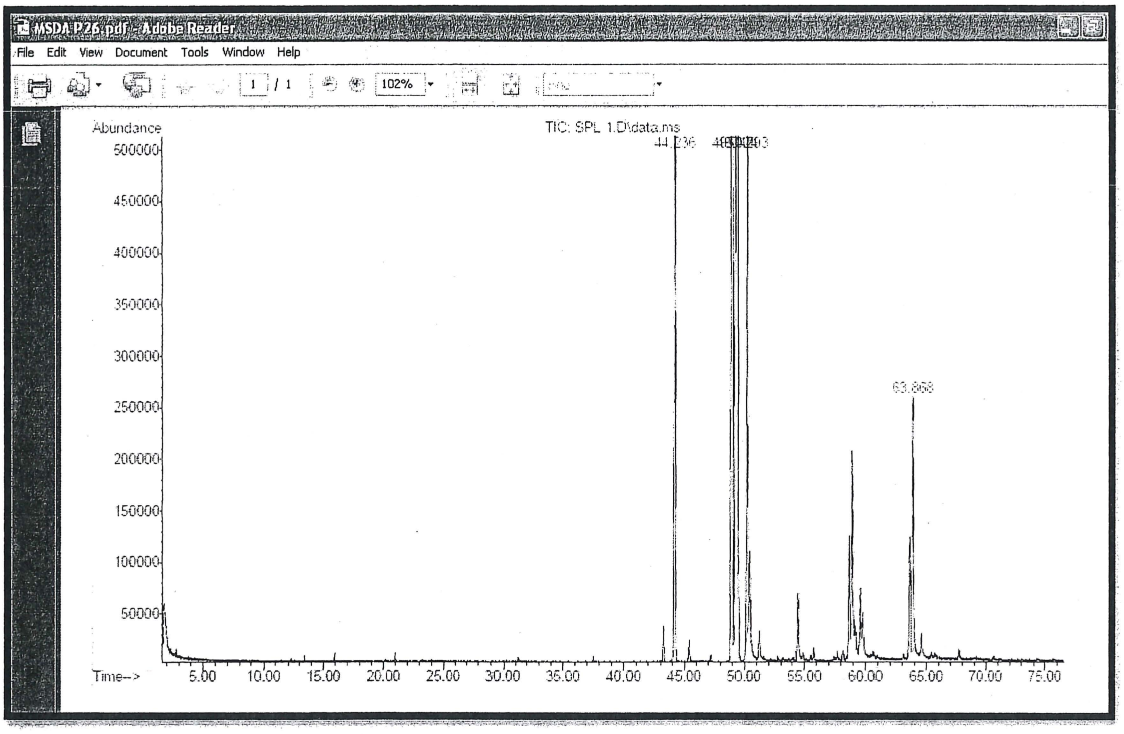
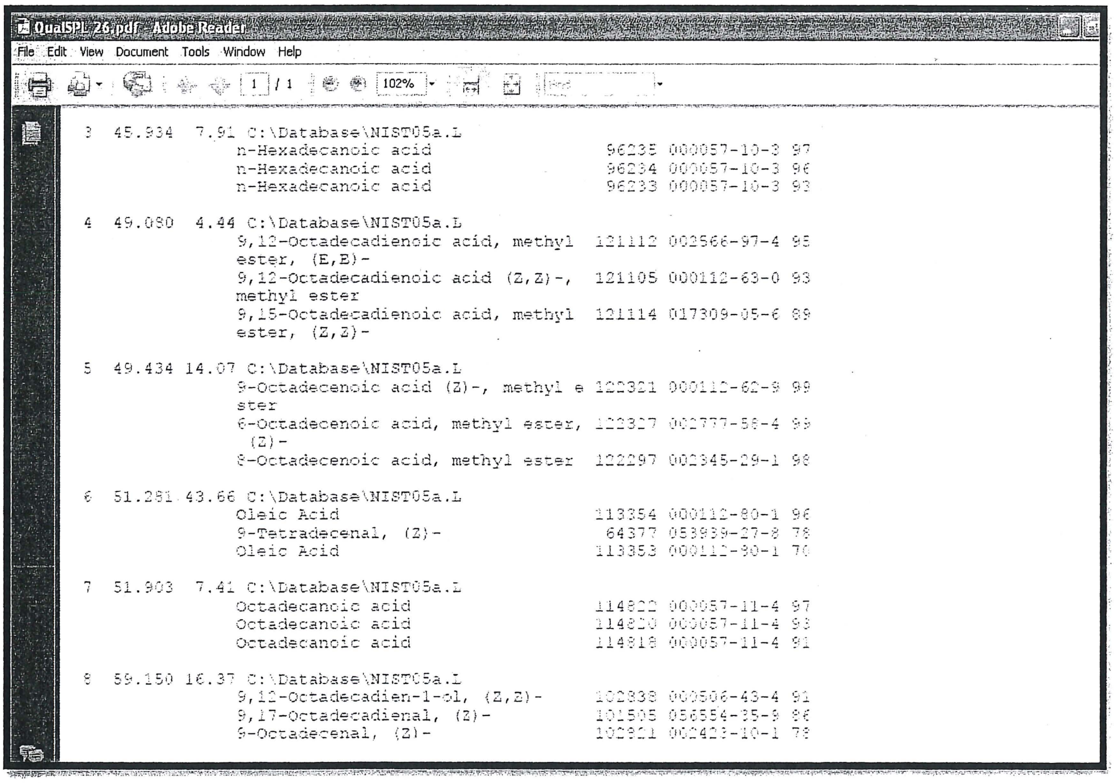
APPENDIX A27 (PRODUCT 26)





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                n-Hexadecanoic acid                  96235 000057-10-3 97
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                n-Hexadecanoic acid                  96233 000057-10-3 93

4  49.080  4.44 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 95
                ester, (E,E)-
                9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 93
                methyl ester
                9,15-Octadecadienoic acid, methyl  121114 017309-05-6 89
                ester, (Z,Z)-

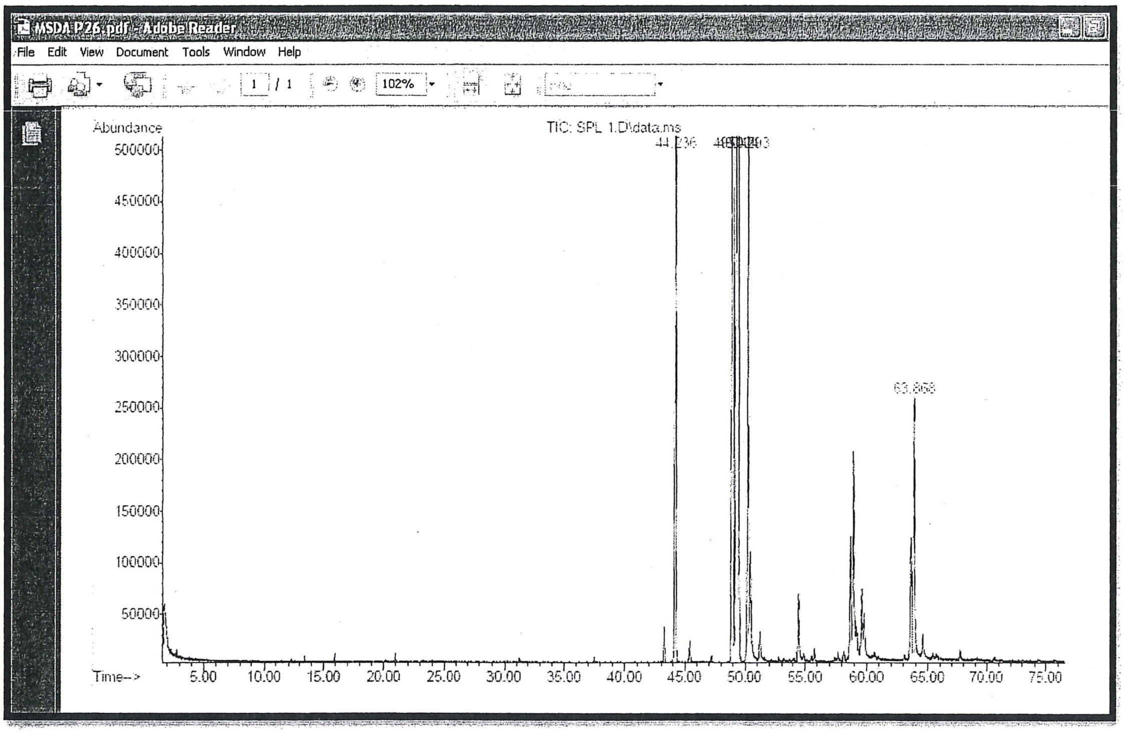
5  49.434 14.07 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                ster
                6-Octadecenoic acid, methyl ester, 122327 002777-58-4 99
                 (Z)-
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 98

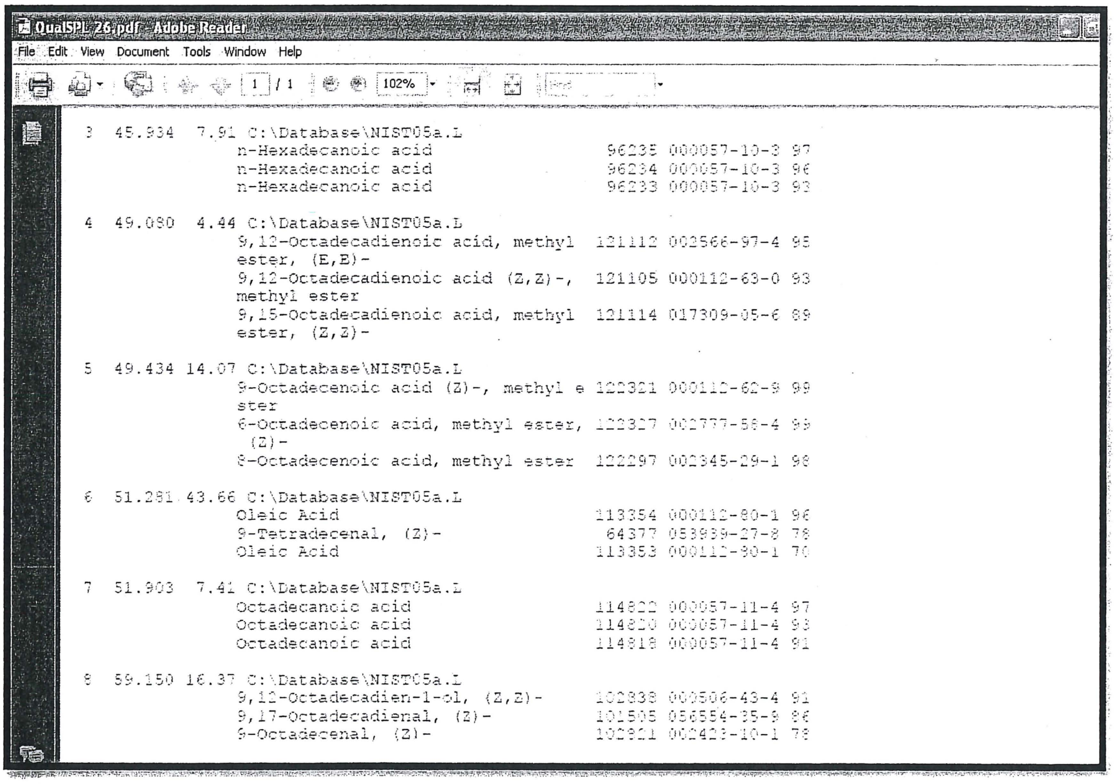
6  51.281 43.66 C:\Database\NIST05a.L
                Oleic Acid                          113354 000112-80-1 96
                9-Tetradecenal, (Z)-                 64377 053939-27-8 78
                Oleic Acid                          113353 000112-80-1 70

7  51.903  7.41 C:\Database\NIST05a.L
                Octadecanoic acid                   114822 000057-11-4 97
                Octadecanoic acid                   114820 000057-11-4 93
                Octadecanoic acid                   114818 000057-11-4 91

8  59.150 16.37 C:\Database\NIST05a.L
                9,12-Octadecadien-1-ol, (Z,Z)-      102838 000506-43-4 91
                9,17-Octadecadienal, (Z)-           101505 056554-35-9 86
                9-Octadecenal, (Z)-                 102921 002423-10-1 78
```

APPENDIX A27 (PRODUCT 26)





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                n-Hexadecanoic acid                  96233 000057-10-3 93

4  49.080  4.44 C:\Database\NIST05a.L
                9,12-Octadecadienoic acid, methyl  121112 002566-97-4 95
                ester, (E,E)-
                9,12-Octadecadienoic acid (Z,Z)-,  121105 000112-63-0 93
                methyl ester
                9,15-Octadecadienoic acid, methyl  121114 017309-05-6 89
                ester, (Z,Z)-

5  49.434 14.07 C:\Database\NIST05a.L
                9-Octadecenoic acid (Z)-, methyl e 122321 000112-62-9 99
                ster
                6-Octadecenoic acid, methyl ester, 122327 002777-58-4 99
                 (Z)-
                8-Octadecenoic acid, methyl ester  122297 002345-29-1 98

6  51.281 43.66 C:\Database\NIST05a.L
                Oleic Acid                         113354 000112-80-1 96
                9-Tetradecenal, (Z)-                64377 053939-27-8 78
                Oleic Acid                         113353 000112-80-1 70

7  51.903  7.41 C:\Database\NIST05a.L
                Octadecanoic acid                  114822 000057-11-4 97
                Octadecanoic acid                  114820 000057-11-4 93
                Octadecanoic acid                  114818 000057-11-4 91

8  59.150 16.37 C:\Database\NIST05a.L
                9,12-Octadecadien-1-ol, (Z,Z)-     102838 000506-43-4 91
                9,17-Octadecadienal, (Z)-          101505 056554-35-9 86
                9-Octadecenal, (Z)-                102921 002423-10-1 78
```

APPENDIX B

Fatty Acids, common name and Abbreviations

Fatty acid	Common Name	Abbreviation
Butanoic acid	Butyric acid	C4:0
Decanoic acid	Caproic acid	C10:0
Dodecanoic acid	Lauric acid	C12:0
Tetradecanoic acid	Myristic acid	C14:0
Hexadecanoic acid	Palmitic acid	C16:0
Hexadecenoic acid	Palmitoleic acid	C16:1
Octadecanoic acid	Stearic acid	C18:0
cis-9-Octadecenoic acid	Oleic acid	C18:1- *cis* (n9)
trans-9-Octadecenoic acid	Elaidic acid	C18:1- *trans* (n9)
all *cis*-9,12-Octadecadienoic acid	Linoleic acid	C18:2 - *cis* (n6)
all *trans*-9,12-Octadecadienoic acid	Linolelaidic acid	C18:2 - *trans* (n6)
all *cis*-9,12,15-Octadecatrienoic acid	α-Linolenic acid	C18:3 (n3)
all *cis*-6,9,12-Octadecatrienoic acid	γ-Linolenic acid	C18:3 (n6)
Eicosanoic acid	Arachidic acid	C20:0
cis-11-Eicosenoic acid		C20:1 (n9)
all *cis*-11,14-Eicosadienoic acid		C20:2 (n6)
all *cis*-11,14,17-Eicosatrienoic acid		C20:3 (n3)
all *cis*-8,11,14-Eicosatrienoic acid	Dihomogammalinolenic acid	C20:3 (n6)
all *cis*-5,8,11,14-Eicosatetraenic acid	Arachidonic acid	C20:4 (n6)
all *cis* 5,8,11,14,17-Eicosapentenoic acid	EPA	C20:5 (n3)
Docosanoic acid	Behenic acid	C22:0
cis-13-Docosenoic acid	Erucic acid	C22:1 (n9)
all *cis*-7,10,13,16-Docosatetraenoic acid		C22:4 (n6)
all *cis* 4,7,10,13,16,19-Docosahexenoic acid	DHA	C22:6 (n3)
Tetracosanoic acid	Lignoceric acid	C24:0
cis-15-tetracosenoic acid	Nervonic acid	C24:1 (n9)