SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF BIO-DIESEL FROM VEGETABLE OILS

ISLAMABAD

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by

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IN THE NAME OF ALLAH

LZ Creations

THE MOST MERCIFUL
THE MOST BENEFICENT
THE MOST COMPASSIONATE
FOR THOSE WHO BELIVE IN ALLAH,
NO ARGUMENT IS NECESSARY
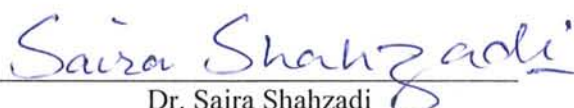AND FOR THOSE WHO DO NOT BELIVE IN ALLAH,
NO ARGUMENT IS POSSIBLE

DECLARATION

This is to certify that this dissertation entitled "*Synthesis and Physico-Chemical Characterization of Bio-Diesel from Vegetable Oils*" submitted by *Mr. Muhammad Tariq* is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, as satisfying the partial requirement for the degree of *Master of Philosophy* in *Analytical/Inorganic Chemistry*.

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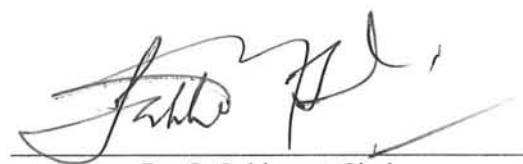Department of Chemistry
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DEDICATION

I dedicate this humble effort to my

Late Father

and

My Loving Mother

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ACKNOWLEGEMENTS

ABSTRACT

Biodiesel was synthesized from vegetable oils by base-catalyzed transesterification with methanol in the presence of NaOH. The optimization of experimental parameters was established to achieve the maximum yield of product. The physical and fuel properties of biodiesel like dynamic viscosity, kinematic viscosity, acid number, density, flash point, cetane number, cloud point and pour point were determined and found comparable to ASTM standards. Prepared biodiesel was chemically characterized by FT-IR, NMR (^{1}H & ^{13}C) and GC-MS to elucidate the identification, quantification and chemical composition. The synthesis of biodiesel was confirmed by comparison of FT-IR and NMR (^{1}H & ^{13}C) analysis of oil and biodiesel. GC-MS analyses identified the chemical compositions of FAMEs in biodiesel and were verified by retention time data and mass fragmentation pattern.

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LIST OF ABBREVIATIONS

RSOB   Rocket seed oil biodiesel

SOB   Sesame oil biodiesel

LSOB   Linseed oil biodiesel

FAMEs   Fatty acid methyl esters

GC-MS   Gas chromatography and mass spectrometry

HSD   High speed diesel

ASTM   American society for testing materials

CHAPTER − 1

INTRODUCTION

Chapter-1

INTRODUCTION

In the last few decades, fuel needs have increased exponentially. In addition, there are several economical, political and environmental problems associated to the use of fuel. Recent petroleum crisis, increasing cost and unavailability of petroleum diesel gave impetus to the scientists to work an alternative fuel. Therefore, in the last years, general awareness about renewable energies, with lower environmental impact, has increased ideally, these alternative should be economically competitive, technically achievable and environment friendly and with high avalailability. As a result, in the near future, the use of renewable energies such as biofuels, biomass, wave, wind and solar energies will have to be wide spread, in order to decrease the dependent of diesel fuels. Biodiesel appears as one of the main alternatives to diesel fuel [1,2].

1.1 History of Vegetable Oil as Fuel

The use of vegetable oil as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel (1858-1913) first tested peanut oil in his compression ignition engine [3], as he demonstrated at the world Exhibition in Paris in 1900. Rudolph Diesel's prime model, a single 10 ft (3 m) iron cylinder with a fly wheel at its base, ran on its own power for the first time in Augsburg, Germany, on August 10, 1883. In remembrance of this event, August 10 has been declared "International Biodiesel Day." In a 1912 speech Diesel said, "the use of vegetable oils for engine fuel may seem insignificant today but such oils may became, in the course of time as important as petroleum and the coal-tar products of the time." Despite the wide spread use of diesel petroleum-desired fuels, interest in vegetable oils as fuels in internal combustion engines is reported in several countries during the 1920 and 1930's and later during World War 11, Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan and China have been reported to have tested and used vegetable oils as diesel fuels during this time. During World War II, experimented with using several different vegetable oils in a Perkins P 6 diesel engine with great success [4]. The

results of this experiment showed that vegetable oils could be used to power a vehicle under normal operating conditions. However, it was noted that much more work was needed before vegetable oils could be used as a reliable substitute for diesel fuel.

The Southwest Research Institute evaluated the chemical and physical properties of 14 vegetable oils [5]. These injection studies pointed out that the oils behave very differently from petroleum-based fuels. This change in behavior was attributed to the vegetable oils' high viscosity. Engine tests showed that carbon deposits in the engine were reduced if the oil was heated prior to combustion. It was also noted that carbon deposit levels differed for oils with similar viscosities, indicating that oil composition was also an important factor.

The characteristic properties of eleven vegetable oils were studied in 1981 to determine which oil would be best suited for use as an alternative fuel source [6]. Of the eleven oils tested, corn, rapeseed, sesame, cottonseed, and soybean oils had the most favorable fuel properties.

The use of sunflower seed oil as a renewable energy source was studied in 1980 [7]. Sunflower oil was tested as a replacement for diesel fuel in agricultural tractors [8]. When operating tractors with 100% sunflower oil instead of diesel fuel, an 8% power loss occurred after 1000 hours of operation. The power loss was corrected by replacing the fuel injectors and injector pump. After 1300 hours of operation, the carbon deposits in the engine were reported to be equivalent to an engine fueled with 100% diesel except for the injector tips, which exhibited excessive carbon build-up. Sunflower oil viscosity was 14% higher than diesel fuel at 37°C. Engine performance using the sunflower oil was similar to that of diesel fuel, but with a slight decrease in fuel economy. Oxidation of the sunflower oil left heavy gum and wax deposits on test equipment, which could lead to engine failure.

In Germany, rapeseed oils were used as a diesel fuel replacement with mixed results [9]. Short-term engine tests indicated rapeseed oil had similar energy outputs when compared to diesel fuel. Initial long-term engine tests showed that difficulties arose in engine operation after 100 hours due to deposits on piston rings, valves and injectors. The investigators indicated that further long-term testing was needed to determine if these difficulties could be adverted.

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In other study, rapeseed oil was used to study the effects of using an alternative fuel in diesel engines [10]. An analysis of the rapeseed oil showed a relationship between viscosity and fatty acid chain length. Engine power and torque results using rapeseed oil were similar to that of diesel fuel. Results of the short-term tests indicated further long-term testing was needed to evaluate engine durability when rapeseed oil was used.

The sunflower, safflower and rapeseed oils were evaluated as possible sources for liquid fuels [11]. The vegetable oils were found to contain 94% to 95% of the energy content of diesel fuel, and to be approximately 15 times as viscous. Short-term engine tests indicated that for the vegetable oils power output was nearly equivalent to that of diesel fuel, but long-term durability tests indicated severe problems due to carbonization of the combustion chamber.

The engine performance tests using raw sunflower and cottonseed vegetable oils as alternative fuels gave poor results [12]. Engine performance tests for processed vegetable oils produced results slightly better than similar tests for diesel fuel. However, carbon deposits and lubricating oil contamination problems were noted, indicating that these oils are acceptable only for short-term use as a fuel source.

Short and long-term engine performance tests were done using 100% soybean oil in a small diesel engine [13]. Short-term test results indicated the soybean performance was equivalent to that of diesel fuel. However, long-term engine testing was aborted due to power loss and carbon buildup on the injectors.

Over 30 different vegetable oils have been used to operate compression engines since the 1900's [14]. Studies involving the use of raw vegetable oils as a replacement fuel for diesel fuel indicate that a diesel engine can be successfully fuel with 100% vegetable oil on a short-term basis. However, long-term engine durability studies show that fueling diesel engines with 100% vegetable oil causes engine failure due to engine oil contamination, stuck piston rings, and excessive carbon build-up on internal engine components. Therefore 100% unmodified vegetable oils are not reasonable diesel fuel replacements.

1.2 Vegetable Oil, Diesel Blends as Potential Fuel Sources

Studies in New Zealand [15] indicated that vegetable oils, particularly rapeseed oil, could be used as a replacement for diesel fuel. Their initial short-term engine tests showed that a 50% vegetable oil fuel blend had no adverse effects. While in long-term tests they encountered injector pump failure and cold starting problems. Carbon deposits on combustion chamber components was found to be approximately the same as that found in engines operated on 100% diesel fuel. These researchers concluded that rapeseed oil had great potential as a fuel substitute, but that further testing was required.

Deere and Company studied the effects of mixing peanut oil and sunflower oil with Number 2 diesel fuel in a single cylinder engine [16]. The vegetable oil blends were observed to increase the amount of carbon deposits on the combustion side of the injector tip when compared with 100% diesel fuel. The vegetable oil fuel blends were found to have a lower mass-based heating value than that of diesel fuel. Fuel filter plugging was noted to be a problem when using crude vegetable oils as diesel fuel extenders.

International Harvester Company reported that cottonseed oil [17], diesel fuel blends behaved like petroleum-based fuels in short-term performance and emissions tests. The experimental fuels performed reasonably well when standards of judgment were power, fuel consumption, emissions, etc. However engine durability was an issue during extended use of these fuel blends because of carbon deposits and fueling system problems.

Caterpillar Tractor Co. compared engine performance of direct injection engines to indirect injection engines when fueled with 30% soybean oil, 70% diesel fuel [18]. The results showed that indirect injection could be operated on this fuel blend while the direct injection engine could not without catastrophic engine failure occurring. The direct injection engines showed injector coking and piston ring sticking as a result of using sunflower oil.

Studies in India were done involving the use of seed oils grown natively in India [19]. Performance tests using fuel blends as great as 50-50 seed oil from the Indian Amulate plant and diesel fuel exhibited no loss of power. Knock free performance with

no observable carbon deposits on the functional parts of the combustion chamber were also observed during these tests.

Studies in Malaysia, with palm oils as diesel fuel substitutes, exhibited encouraging results [20]. Performance tests indicated that power outputs were nearly the same for palm oil, blends of palm oil and diesel fuel, and 100% diesel fuel. Short-term tests using palm oil fuels showed no signs of adverse combustion chamber wear, increase in carbon deposits, or lubricating oil contamination.

Some other studies [21,22] indicated that while vegetable oil fuel blends had encouraging results in short term testing, problems occurred in long-term durability tests. They indicated that carbon build-up, ring sticking, and lubricating oil contamination was the cause of engine failure when vegetable oils were used in high percentages (50% or more) as diesel fuel substitutes.

Due to engine durability problems encountered using raw vegetable oils as a fuel in the early 1980's, most researchers opted to use chemically modified vegetable fuels more commonly known as biodiesel in place of unrefined vegetable oils.

Another attempt to overcome the problems of high viscosity of oil was pyrolysis and cracking of the oils [23-32]. Thermal cracking, or controlled pyrolysis, of bio-oil decrease its molecular weight and is thereby effective in converting oil to a more useable fuel, like biodiesel [33]. Some other work on pyrolysis of soy, palm and castor oils were done in Brazil [34].

1.3 History of Biodiesel

Biodiesel is the nonpetroleum-based mono-alkyl esters of long chain fatty acid derived from renewable feed stock such as vegetable oil or animal fats. Biodiesel is commonly composed of methyl or ethyl esters that can be prepared from triglycerides in vegetable oils by transesterification with low molecular weight alcohols (methanol or ethanol) in the presence of base catalyst [35]. Chemically the oils/fats consist of triglycerides molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double binds in these chains. Biodiesel molecules contain no sulfur, ring molecules or aromatics. Biodiesel is thus essentially free of sulphur and

aromatics. Biodiesel is made up of almost 10% oxygen, making it a naturally "oxygenated" fuel.

The first remarkable work on biodiesel was performed in Belgium and its former colony the Belgian Congo (known after its independence for a long time as Zaire. Belgian Patent 422, 87, granted on Aug. 31, 1937, to G. Chavanne (of the university of Brussels), constitutes the first report on what is today known as biodiesel. It describes the use of ethyl esters of palm oil as diesel fuel. These esters were obtained by acid-catalyzed transesterification of the oil. A bus fueled with palm oil ethyl esters served the commercial passenger line between Brussels and Lou vain (Leuven) in the summer of 1938. Performance of the bus operating on that fuel reportedly was satisfactory. It was noted that viscosity difference between the esters and petro-diesel was considerably les than that between the patent oil and petro-diesel fuel. The cetane number of palm oil ethyl esters was reported as approximately 83 (relative to a high quality standard of cetane number 70.5 and a low quality standard of cetane number 18 and diesel fuels with cetane number of 50 and 57.5.

In the mid 1970s, fuel shortage spurred interest in diversifying fuel resources and thus biodiesel was developed as an alternative to petro-diesel. Use of methyl esters of sunflower oil to reduce the viscosity of vegetable oil was reported at several technical conferences in 1980 and 1981 and marks the beginning of the discovery and eventual commercialization of biodiesel. The term biodiesel was first time used in a Chinese paper published in 1988. The next paper using that term appeared in 1991 and from then on the use of the term "biodiesel" in the literature has expanded exponentially.

In the United States, energy security and reduction of exhaust emission drove a force to use vegetable oil-based diesel fuels. So the clean Air Act Amendments in 1990 and the Energy Policy Act of 1992 mandate the use of alternative, or "clean", fuels in regulated truck and bus fleets. Ammendments to the Energy Policy Act enacted into the law in 1998, which provide credits for biodieel use and blends with petro-diesel. In the United States 10 percent of all federal vehicles were to be using alternative fuels to set an example for the private automotive and fuel industries. In USA and Brazil, soybean oil is the principal oil being utilized for biodiesel.

In Europe, biodiesel has been produced on an industrial scale in the European Union since 1992, largely in response to positive signals from the EU institutions. The EU council of ministers adopted new Pan-EU rules for detaxation of biodiesel and fuels on October 27, 2003. Today, there are approximately 120 plants in the EU producing up to 6.1 million tones of biodiesel annually. These plants are mainly located in Germany, Italy, France, Austria and Sweden.

In India, researchers provoked by the events of World War 11, extended their investigation on ten vegetable oils for development as a domestic fuel. Work on vegetable oils as diesel fuel ceased in India when petroleum based diesel fuel again became available plentiful at low cost. Now India Jatropha plant is one of the important sources of biodiesel.

1.4 Sources of biodiesel

Biodiesel is produced from various vegetable oils through a chemical process called transesterification where by glycerin is separated from the oil [36-58]. Various sources of biodiesel in different countries of the world are;

Soyabean oil	USA
Soyabean oil	Brazil
Rapeseed oil	Germany
Sunflower oil	France
Sunflower oil	Italy
Palm oil	Malaysia
Palm oil	Indonesia
Olive oil	Spain
Jatropha oil	India
Guang pi	China

1.5 Biodiesel Benefits

Biodiesel is the name of a clean burning alternative fuel, produced from domestic renewable resources. It can be used in compression-ignition engine without any modification. It can be used as pure B100 or can be blended with petro-diesel. The application can be broadly categorized into three portions.

1.5.1 Environment

Biodiesel has been demonstrated to have significant environmental benefits. Biodiesel is non-toxic, biodegradable [59]. It reduces the emission of harmful pollutants (mainly particulates) from diesel engines [60]. It reduces 80-90% CO_2 emission. It is extremely low in sulpher (100% less sulfur dioxide). It has a high lubricity and fast biodegradability. It has a high cetane number (above 100, as compared to only 40 for diesel fuel). Cetane number is a measure of a fuel's ignition quality. The high cetane number is a measure of a fuel's ignition quality. The high cetane number of biodiesel contributes to easy cold starting and low idle noise. Its use can extend the life of diesel engines because it is more lubricating [61] and, furthermore, power output are relatively unaffected by biodiesel.

1.5.2 Agricultural benefits

Biodiesel stimulates agriculture and can be locally grown. In those countries, where agriculture is a key economic factor, biodiesel is attractive to farmers as a new income generator and for industry revitalization.

1.5.3 Energy security

Biodiesel reduces dependence on imported crude oil or refined products. It is a part of alternative solution. It rapidly increases domestic oil security. Biodiesel makes our country less dependent on expensive foreign oil and helps the economy.

1.6 Vegetable oils used in present research

1.6.1 Rocket seed oil (*Eruca sativa* Miller)

Rocket seed plant is also called rocket, true rocket, rocket salad, Arugula, Boquette or white pepper. Rocket is high in erucic acid (C22:1) and oleic acid (C18:1). Rocket seed plant is well known for its outstanding draught tolerance, as a result it plays an important role in oilseed production in arid and semi-arid regions around the world.

Rocket seeds contain 34% oil contents. Rocket seed oil is mainly used in industries as a lubricant, for soap-making, as an illuminating agent, in medicines and in cooking as a salad oil. High erucic acid oil has high flash point, oiliness and stability at high temperature, ability to remain fluid at low temperature and durability. So rocket seed oil can be effectively used for biodiesel production.

1.6.2 Sesame oil (*Sesamum indicum*)

Sesame is an annual self pollinating plant with an erect, pubescent, branching stem, and 0.60 to 1.20 m tall. In addition, the flowers are borne on short glandular pedicels. The fruit is an oblong, mucronate, pubescent capsule containing numerous small, oval, and yellow, white, red, brown, or black seeds. Sesame oil (also known as gingelly oil and till oil) is an organic oil, noted to have the distinctive aroma and taste of its parent seed. Sesame seeds contain 45% oil contents. It is an important group of agricultural commodity in terms of value in the world trade and play an important role in international market.

1.6.3 Linseed oil (*Linum usitatissimum*)

Linseed is an annual herb with erect, slender stems, 60-80 cm tall. A cultivated plant in closely spaced field conditions it has little branching except at the apex. The seeds are oval, somewhat flattened, 4-6 mm long and are pale to dark brown and shiny. Linseed oil, also known as "flax seed oil" is a clear to yellowish oil obtained from the dried ripe seeds of the flax plant *(Linum usitatissimum)*. It is an edible oil, but because of its strong flavor and odor is only a minor constituent of human nutrition. Linseeds contain 45% oil contents. Linseed is predominantly grown as a source of oil for industrial use in the manufacture of paints, varnishes and linoleum.

1.7 Objectives

Presently the world's energy needs are met through non-renewable resources such as petrochemicals, natural gas and oil. Pakistan is also fully dependent on the above resources and consumed a big part of its GDP on the import of petroleum. In Pakistan now a day, efforts are being made to explore alternative sources of energy. An alternative fuel must be technologically feasible, economically competitive, environmentally acceptable and readily available [62].

Fatty acid methyl esters (FAMEs), the chemical name of a biodiesel derived from renewable sources such as vegetable oils has gained importance. It is the need of the time to explore potential oil seeds for practical implementation of biodiesel in Pakistan. In this context the present research is based on the following objective:

- To identify the oil rich species for biodiesel production.
- To characterize the biodiesel physico-chemically by different analytical techniques like FT-IR, NMR, GC-MS etc.
- In the long run, to reduce dependence of Pakistan on imported crude oil.
- To develop a suitable and viable process toward commercialization of biodiesel and biodiesel blend in Pakistan.

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CHAPTER — 2

PHYSICO – CHEMICAL CHARECTERIZATION

Chapter-2

PHYSICO-CHEMICAL CHARACTERIZATION

2.1 Viscosity

Viscosity is a measure of the internal friction or resistance of an oil to flow. Viscosity is measured on several different scales such as Ostwald viscometer and Ubbelohde viscometer. The number of seconds required for an oil or biodiesel to flow out of a standard Ubbelohde viscometer at a definite temperature.

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperature 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. According to ASTM standard (D 6751) acceptable viscosity @ 40 °C range for biodiesel to be 1.9-6.0 mm^2/s [1].

2.2 Density

Density is the weight of a unit volume of fluid. Density is an important parameter for diesel fuel injection systems. It is desirable to maintain diesel density within a tight tolerance to achieve optimal air to fuel ratios. The upper density limit also reduces the heavy aromatics and high molecular weight paraffin. Biodiesel tends to have density in the range 0.82-0.88 g/cm^3 [2,3].

2.3 Specific gravity

Specific gravity is the ratio of the density of the liquid to the density of water. Specific gravity of biodiesel ranges between 0.86-0.90 g/cm^3 depending on the feedstock used [4].

2.4 Acid number

Acid number is the number of milligram of KOH used to neutralize one gram of sample oil. Acid number is a measure of Free Fatty acid in oil and biodiesel. The percentage of acid number in biodiesel greater than 3% can cause operational problems such as corrosion and pump plugging by deposit formation. 0.5 mg of acid number equalizes 1% Free Fatty Acid. The transesterification would not occur if oils with FFA contents of > 3% were used [5].

Acid number was determined by acid-base titration using phenolphthalein as an indicator and isopropyl alcohol as solvent. Non-edible crude oil contains more Free Fatty Acid as compared to edible oils.

2.5 Cetane number

Cetane number is the ability of fuel to ignite quickly after being injected. Better ignition quality of the fuel is always associated with higher CN value. This is an important parameter related to the ignition delay time and combustion quality. CN is based on two compounds, namely hexadecane with a cetane of 100 and heptamethylnonane (HMN) with a cetane of 15. The CN scale also shows that straight chain, saturated hydrocarbons have higher CN compared with branched chain or aromatic components of similar molecular weight and number of carbon atoms. The high CN employs short ignition delay. The longer the fatty acid carbons and the more saturated the molecules the higher the CN. The CN of biodiesel from animal fats is higher than those of vegetable oils. Different countries/ organizations have specified different minimum values. Biodiesel of USA (ASTM D 6751), Germany (DIN V51606) and European organization (EN 14214) has set this value as 47, 49 and 51 respectively [6].

2.5.1 Cetane number enhancers

The structure dependent ignition delay time of a fuel can be influenced by compounds known as cetane improver, which raise CN. Cetane improves have been identified for fatty compounds that occur in biodiesel [7].

Cetane improvers may have another important ramification, namely the reduction of NO_x exhaust emissions. It is known for petrodiesel that cetane improvers can reduce these exhaust emissions [8].

2.6 Flash Point

Flash point is the temperature at which a substance given off sufficient vapours to produce a momentary flash. OR Flash point is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame. Flash point of biodiesel is greater than petrodiesel.

Higher flash point of biodiesel ensures more safety in the handling and storage. So it is a safer fuel than petro-diesel [9].

2.7 Cloud point

The temperature at which oil starts to solidify is known as cloud point. OR Cloud point is the temperature at which crystals of biowax first appear. Crystals can be detected by cloudiness of the fuel. Biodiesel has higher cloud point as compare to HSD [10]. Biodiesel cloud point is dependent on the composition of the esters and can range from -3 °C to +11 °C. As the temperature is lowered, the crystals continue to grow until the oil is no longer a fluid but a solid. The presence of crystals or solidified wax thickens the oil and clogs fuel fillers and injectors in engines.

When the fuel nears the cloud point temperature, changes will need to be made to the fuel, such as the addition of anti-gel additives, kerosene oil and petr-odiesel. The addition of fuel line heaters is another excellent method to prevent gelling of biodiesel fuel.

2.8 Pour point

The pour point of a liquid is the lowest temperature at which it will pour or flow under prescribed conditions.

Pour point is a measure of the fuel gelling temperature, at which point the fuel can no longer be pumped. The pour point is always lower than the cloud point. Biodiesel cold temperature gelling properties greatly differ from feedstock to feedstock. Best results are seen with biodiesel produced from unsaturated oils. Like any diesel fuel, biodiesel can gel at low temperatures. Some types of biodiesel freeze at higher temperatures than others, depending on the level of saturated components in the fuel. Pure biodiesel should be stored at temperatures at least 15 degrees higher than the pour

point of the fuel (30 °F to 56 °F). A storage temperature of 45 °F to 50 °F is fine for most B100. Blends of biodiesel and diesel should be stored at temperatures of at least 15 degrees above the pour point of the blended fuel.

Diesel and kerosene are common pour point additives that reduce the fuel gelling temperature signicantly. Some other pour point depressants are Malan-Styrene esters (MSC), Polymethacrylate (PMA) and Ethylene Vinyl Acetate (EVA).

2.9 Vibrational spectroscopy

Infrared region lies on the immediate low energy side of visible spectrum. It is one of the most applied analytical techniques which have been used to monitor the quality of biodiesel and petrodiesel blends [11]. The biodiesel was characterized in range of 4000-400 cm^{-1} by means of spectral comparison of raw oil and the biodiesel B100.

2.10 Multinuclear NMR

NMR is a versatile spectroscopic method that has become one of the most powerful techniques to elucidate the structure of chemical compounds. It is an extremely important technique for structural analysis and quantification of fatty acid methyl esters.

2.10.1 ^{1}H NMR

^{1}H NMR is frequently used to follow the biodiesel synthesis [12-15]. It is used to quantify the conversion of vegetable oils in methyl esters by transesterification reaction [16]. Deuterated chloroform (CDCl$_3$) is the most commonly used solvent. ^{1}H NMR provides following information.

1) Chemical shift of peak which shows the environment of proton involved.

2) Intensities of individual peaks which corresponds to the number of protons.

3) Multiplicity that tells about number of neighboring protons.

2.10.2 ^{13}C NMR

^{13}C NMR spectra are based on natural ^{13}C, which occurs at a level of 1.1% in organic compounds. The spectra provide two kinds of information.

1) The chemical shift of each signal

2) Their relative intensities

The former is of qualitative value and permits identification of important structural features, the latter, provides quantitative information of analytical value.

^{13}C NMR spectra of seed oils and biodiesel provide useful information about confirmation of FAMEs and their composition. In biodiesel, a mixture of FAMEs present so many individual signals will be replaced by clusters [17].

2.11 Gas Chromatography- Mass Spectrometry

GC-MS is effectively used for the analysis of FAMEs in biodiesel. The FAMEs are separated based on the boiling point (chain length) difference by a non-polar chromatography column and are identified by fragmentation using a hard ionization MSD technique such as electron impact (EI) ionization [18]. The sample is carried by inert gas through the instrument. The inert gas is usually helium.

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CHAPTER — 3

EXPERIMENTAL

Chapter-3

EXPERIMENTAL

3.1 Chemicals

All of the chemicals used in the research work were of high purity. The following chemicals for biodiesel synthesis and physico-chemical characterization were purchased and used without any further purification.

- Methanol (CH_3OH),   Merck
- Sodium hydroxide (NaOH),   Merck
- Potassium hydroxide (KOH),   Merck
- Isopropyl alcohol (C_3H_7OH),   Merck
- Toluene ($C_6H_5CH_3$),   Aldrich
- Sodium sulphate (Na_2SO_4),   Merck
- Acetic acid (CH_3COOH),   Riedel-de-Haen
- Oxalic acid ($C_2O_4H_2 . 2H_2O$),   Fluka

3.2 Instrumentation

Dynamic viscosity and kinematic viscosity were determined by an Ubbelohde viscometer. Density was determined by using a specific gravity bottle. Acid number was determined by acid-base titration method using titration apparatus. Biodiesel B100 was analyzed by FT-IR, using a Bio-Rad Excalibur Model FTS3000MX in the range 4000 - 400 cm^{-1}. NMR spectra (^1H and ^{13}C) were recorded in $CDCl_3$ as internal reference by using a Bruker ARX-300MHz FT-NMR. GC-MS analyses were performed using a GC-6890N directly coupled to MS5973MSD. 0.1μL biodiesel B100 in hexane was injected. The carrier gas was Helium with column DB-5MS. The mass spectrometer was set to scan in the range of m/z 02-600 and ionization potential 70 eV. The column temperature was programmed from 120 -300 °C at the rate of 10 °C/min.

3.3 Procedure for the synthesis of biodiesel

3.3.1 Transesterification

Transesterification is the displacements of alcohol from an ester by another alcohol in a process similar to hydrolysis expect that an alcohol is used instead of water [1]. The general reaction is represented as Equation 3.1.

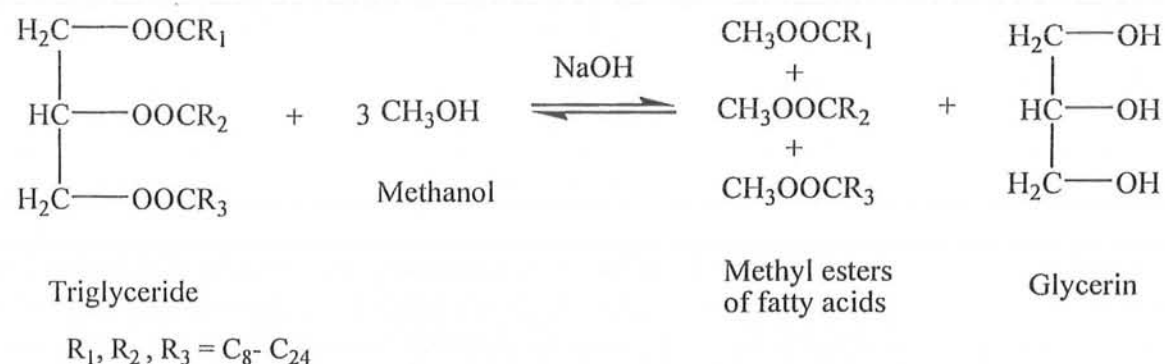$$RCOOR^1 + R^2OH \underset{\text{Catalyst}}{\rightleftharpoons} RCOOR^2 + R^1OH$$

$$\text{ester} \qquad \text{alcohol} \qquad\qquad \text{ester} \qquad \text{alcohol}$$
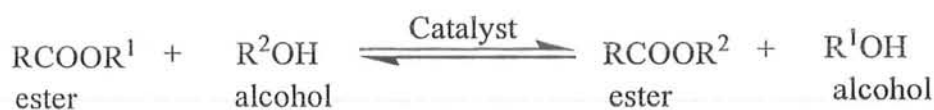
Equation 3.1. General equation of transesterification of esters.

$R^1 = C_8 - C_{24}$

$R^2 = C_1 - C_2$

$R = -CH_2(O)-CH(O)-CH_2(O)-$

Methyl esters were prepared by transesterification according to conditions suggested in the literature [2,3]. The vegetable crude oil was first filtered to remove suspended particles and then preheated up to 120°C to remove moisture on a hot plate before starting the reaction. The sodium methoxide (catalyst) was prepared by mixing 200 ml of methanol and 6.5 g of NaOH in a separate beaker and stirred for half an hour. The sodium methoxide solution was put into one liter of vegetable oil at 60 °C and stirred for 90 min. The mechanism of base catalyzed transesterification is described as Equation 3.2 and the flow chart for transesterification is shown in Fig. 3.1.

$$\begin{array}{llll}
H_2C\text{---}OOCR_1 & & CH_3OOCR_1 & H_2C\text{---}OH \\
| & NaOH & + & | \\
HC\text{---}OOCR_2 \; + \; 3\,CH_3OH & \rightleftharpoons & CH_3OOCR_2 \;+\; & HC\text{---}OH \\
| & & + & | \\
H_2C\text{---}OOCR_3 & \text{Methanol} & CH_3OOCR_3 & H_2C\text{---}OH \\
\end{array}$$

Triglyceride   Methyl esters   Glycerin
                       of fatty acids

$R_1, R_2, R_3 = C_8 - C_{24}$

Equation 3.2. Equation for transesterification of triglycerides

Then after the reaction, the system was cooled to room temperature and allowed to settle down, resulting in the separation of two phases. The upper phase contained biodiesel and lower phase contained glycerin by-product, the product biodiesel was separated from glycerin by simple decantation. Crude biodiesel contains the excess

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methanol, the remaining catalyst together with the soap formed during the reaction and some entrained methyl esters and partial glycerides.

3.3.2 Methyl esters wash

After separation of the two layers, the upper biodiesel layer was purified by distilling the residual methanol at 60 °C. The remaining catalyst was removed by successive rinses with distilled water at pH 4.5 by adding 1-2 drops of acetic acid. Finally, the residual water was eliminated by treatment with anhydrous Na_2SO_4, followed by filtration.

3.3.3 Glycerin purification

The lower phase was acidified by acetic acid to neutralize any untreated NaOH and decompose the soap formed during transesterification. The resulting mixture was subjected to distillation to remove excess methanol. This facilitated the separation of entrained methyl esters and soaps.

3.3.4 Biodiesel yield

The biodiesel yield can be calculated by

$$\text{Yield of methyl esters} = \frac{\text{gram of methyl esters produced}}{\text{gram of oil taken for the reaction}} \times 100$$
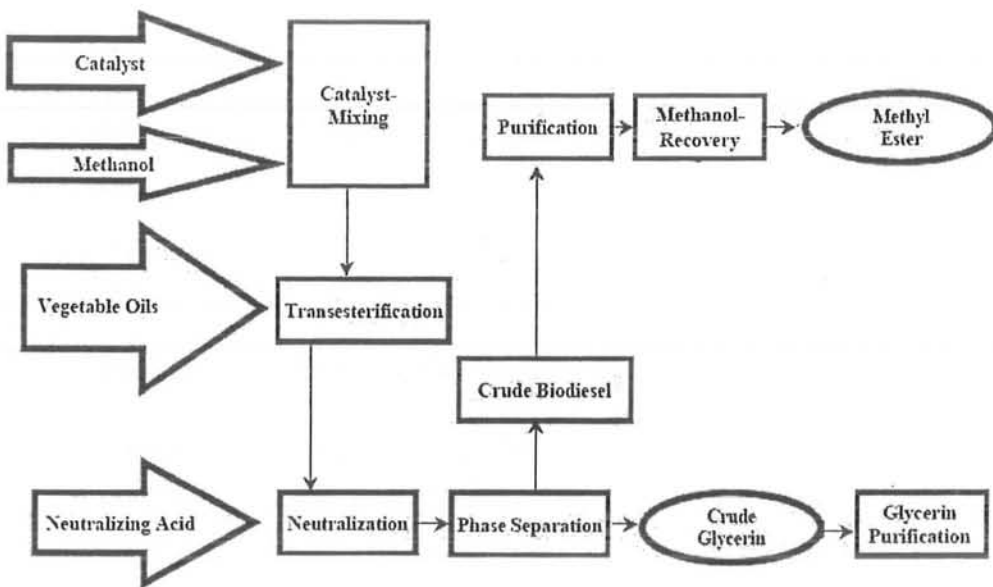

Fig. 3.1. The flow chart for transesterification of vegetable oils

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3.4 Procedure for the determination of density

Density was determined using specific gravity bottle having a volume of 5 ml. The empty bottle was first weighed, using a weigh balance. Then the weight of bottle having oil/biodiesel was determined. The difference between the two weights was the mass of the sample. The density was calculated using the following formula:

$$d = m/v$$

The units for density are g/cm^3 or kg/m^3.

3.5 Procedure for the determination of viscosity

Viscosity was determined using Ubbelohde viscometer. The time of flow of water was taken as a reference. 10 ml of sample was poured into the viscometer using a graduated cylinder. The liquid was sucked upto the point A using the suction pump. Then the liquid was made to fall freely up to the mark B of the viscometer. Time of flow of liquid was noted using a stop watch. This procedure was repeated for three concordant readings, both for sample oil or biodiesel and water. Dynamic viscosity is represented by a Greek letter "η"(eta) and kinematic viscosity by "v". Viscosity was calculated using the formula:

$$\eta_l = \eta_w \ X \ \frac{t_l}{t_w} \ X \ \frac{d_l}{d_w}$$

Where,

η_l = Viscosity of oil / biodiesel

η_w = Viscosity of water

t_l = Time of flow of oil / biodiesel

t_w = Time of flow of water

d_l = Density of oil / biodiesel

d_w = Density of water

Unit,

Dynamic viscosity = Centipoise (cP)

$$\text{Kinematic viscosity} = \frac{\text{Dynamic viscosity}}{\text{Density}}$$

$$v = \frac{\eta}{d}$$

Unit,

$$\text{Kinematic viscosity} = \text{Centistokes (cSt)}$$

3.6 Procedure for acid number determination

Acid number is defined as the number of milligram of KOH used to neutralize one gram of sample oil or biodiesel. Acid number is a measure of FFA (free fatty acid) in oil and biodiesel. Acid number of both oil and biodiesel was determined by aqueous acid base titration. Two types of titrations were performed, blank titration and sample titration. In blank titration only isopropyl alcohol and phenolphthalein indicator were taken in conical flask and titrated against KOH from burette. The end point was violet color. In sample titration isopropyl alcohol, sample (oil or biodiesel) and phenolphthalein indicator were taken in conical flask and titrated against KOH from burette. The end point was light pink color. The acid number is calculated by the following formula.

$$\text{Acid number} = \frac{(A - B)C}{V}$$

Where,

A = Volume of KOH used for sample (mL)

B = Volume of KOH used for blank (mL)

C = Concentration of KOH (g/L)

V = Volume of sample (mL)

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CHAPTER − 4

RESULTS AND DISCUSSION

Chaptet-4

RESULTS AND DISCUSSION

The properties of biodiesel prepared from rocket seed oil, sesame oil and linseed oil are close to petrodiesel. The biodiesel was characterized by determining dynamic viscosity, kinematic viscosity, density, acid number, flash point, pour point, cetane number and chemical characterization by FT-IR, NMR (^{1}H, ^{13}C) and GC-MS. The physical and fuel properties of oil and biodiesel, are given in Tables 4.1- 4.3 and 4.4 respectively.

Table 4.1: Physical properties of rocket seed oil and biodiesel

Parameters	Unit	Rocket seed oil	Rocket seed oil biodiesel	ASTM (Biodiesel specifications)
Dynamic viscosity @ 20°C @ 40°C	cP	77.58 -	9.68 3.88	1.6-4.1@ 40 °C
Kinematic viscosity @ 20°C @ 40°C	cSt	88.05 -	11.44 4.45	1.9-6 @ 40 °C
Density @ 40°C	g/cm^3	0.881	0.87	0.82-0.88
Acid number	mg KOH /g of oil/biodiesel	4.62	0.07	0.5

Table 4.2: Physical properties of linseed oil and biodiesel

Parameters	Unit	linseed oil	Linseed oil biodiesel	ASTM (Biodiesel specifications)
Dynamic viscosity @ 20°C @ 40°C	cP	28.00 -	5.12 3.25	1.6-4.1 @ 40°C
Kinematic viscosity @ 20°C @ 40°C	cSt	30.43 -	5.81 3.83	1.9-6 @ 40°C
Density @ 15°C	g/cm^3	0.88	0.85	0.82-0.88
Acid number	mg KOH /g of oil/biodiesel	2.4	0.21	0.5

Table 4.3: Physical properties of sesame oil and biodiesel

Parameters	Unit	Sesame oil	Sesame oil biodiesel	ASTM (Biodiesel specifications)
Dynamic viscosity @ 40°C	cP	39.6	5.77	1.6-4.1@ 40°C
Kinematic viscosity @ 40°C	cSt	44	6.62	1.9-6@ 40°C
Density @ 40°C	g/cm^3	0.89	0.871	0.82-0.88
Acid number	mg KOH /g of oil/biodiesel	2.7	0.14	0.5

Table 4.4: Fuel properties of RSOB, LSOB and SOB

Biodiesel	Flash Point	Cloud Point	Pour Point	Cetane number
HSD ASTM	60-80	-15 to 5	-35 to -15	40-55
RSOB	110	5	-12	47
LSOB	64	-2	-4	-
SOB	110	-4	-10	53

4.1 Viscosity

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperature 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.

According to ASTM standard (D 6751) acceptable viscosity @ 40 °C range for biodiesel to be 1.9-6.0 mm^2/s. The dynamic and kinematic viscosity comparision of oil and biodiesel for RSOB, LSOB and SOB are given in Table 4.1- 4.3, respectively. The results showed that viscosity of RSOB, LSOB and SOB of are comparable to ASTM standard.

4.2 Density

Biodiesel tends to have density in the range 0.82-0.88 g/cm^3. The density comparison of oil and biodiesel of RSOB, LSOB and SOB are shown in Table 4.1- 4.3, respectively. The values of the densities in the present analysis were quite comparable to those reported in the literature [1,2].

4.3 Acid number

Acid number is a measure of Free Fatty Acid in oil and biodiesel. The percentage of acid number in biodiesel greater than 3% can cause operational problems such as corrosion and pump plugging by deposit formation. 0.5 mg of acid number equalizes 1% Free Fatty Acid. The acid number in RSOB, SOB and LSOB are 0.07, 0.14 and 0.21 mg KOH/g of sample, respectively which is in accordance to ASTM standard.

4.4 Flash Point

The Flash point of biodiesel was higher than mineral diesel. The flash point of RSOB and SOB are shown in Table 4.4 which is higher than mineral diesel and it ensures more safety in the handling and storage. The flash point of LSOB is 64 which is comparable to HSD. A higher degree of flash point decreases the risk of fire.

4.5 Cloud point and Pour point

The values of cloud point (cp) and pour point (pp) of RSOB,LSOB and SOB in this study were also in accordance with ASTM standards (Table 4.4). The cp is the temperature at which biowax first becomes visible when the fuel is cooled. The pp is the temperature at which the amount of wax, out of solution is sufficient to get the fuel, thus it is the lowest temperature at which the fuel can flow. Biodiesel has higher cp and pp as compared to HSD [3].

4.6 Vibrational Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) has become one of the major analytical techniques used because of its quality, screening, quickness and cost of analysis. The biodiesel can be characterized in spectral range of 4000-400 cm^{-1} by means of spectral comparison of raw oil and the biodiesel.

The FT-IR spectral data of rocket seed oil, sesame oil, linseed oil and their biodiesel are given in Table 4.5. The values of oil and biodiesel are very similar since the two compounds have almost same chemical groups. However, some differences are detectable. The position of carbonyl group band in FT-IR is sensitive to substitute effects

and to the structure of the molecule [4]. The methoxycarbonyl group in biodiesel shows a different band position of the υ (-COOR) vibration when compared to the carbonyl band in the oil.

Table 4.5: FT-IR data (cm^{-1}) of rocket seed oil, sesame oil, linseed oil and their biodiesel

Oil	υ(COOR)	υ(C-O)	Biodiesel	υ(COOR)	υC-C(=O)-O and υO-C-C
Rocket seed oil	1747	1157	RSOB	1742	1171 1017
Sesame oil	1745	1159	SOB	1743	1172 1018
Linseed oil	1743	1195	LSOB	1742	1172 1018

The esters have two characteristically strong absorption bands arising from methoxy carbonyl and C-O stretching [5].

The methoxy carbonyl group in rocket seed oil biodiesel changed from 1747 cm^{-1} in oil to a strong band at 1742 cm^{-1} in biodiesel. The C-O stretching vibration in biodiesel showed two asymmetric coupled vibrations, 1171 cm^{-1} due to v C-C(=O)-O and 1017 cm^{-1} due to O-C-C. The methyl group stretching band appeared at 2926 cm^{-1} while methylene stretching band appeared at 2855 cm^{-1}. The methyl groups bending vibrations appeared at 1459 and 1362 cm^{-1} while ρCH$_2$ at 722 cm^{-1}.

The methoxy carbonyl group in sesame oil biodiesel showed a strong band at 1743 cm^{-1}, while C-O stretching vibration showed two asymmetric coupled vibration 1172 cm^{-1} due to v C-C(=O)-O and 1018 cm^{-1} due to O-C-C. The band due to v C-C(=O)-O is broader and stronger than C=O stretching absorption. The methyl group stretching band appeared at 2926 cm^{-1} while methylene stretching band appeared at 2856 cm^{-1}. The methyl group bending vibration appeared at 1459 and 1363 cm^{-1} while ρCH$_2$ at 722 cm^{-1}.

The methoxy carbonyl group in linseed oil biodiesel changed from 1743 cm^{-1} in oil to a strong band at 1742 cm^{-1} in biodiesel. The C-O stretching vibration in biodiesel showed two asymmetric coupled vibrations, 1172 cm^{-1} due to v C-C(=O)-O and 1018 cm^{-1} due to O-C-C. The methyl group stretching band appeared at 2926 cm^{-1} while methylene stretching band appeared at 2856 cm^{-1}. The methyl groups bending vibrations appeared at 1440 and 1362 cm^{-1} while ρCH$_2$ at 720 cm^{-1}.

4.7 Multinuclear NMR Spectroscopy

The NMR is an extremely important technique for structural analysis and quantification of fatty acid methyl esters (FAMEs). The rocket seed oil biodiesel, sesame oil biodiesel and linseed oil biodiesel are characterized by NMR (^{1}H and ^{13}C).

4.7.1 ^{1}H NMR Spectroscopy

The ^{1}H NMR data of rocket seed oil, sesame oil and linseed oil are reported in Table 4.6 and the representative spectra of rocket seed oil and linseed oil are shown in Fig. 4.1 and 4.2. The ^{1}H NMR data of rocket seed oil biodiesel, sesame oil biodiesel and linseed oil are reported in Table 4.7 and the representative spectra are shown in Fig. 4.3-4.5, respectively. The characteristic two peaks, methoxy protons (singlet) and ά-CH$_2$ protons (triplet) are the distinct feature for confirmation of methyl esters present in the biodiesel. ^{1}H NMR can be used to quantify the conversion of vegetable oil in methyl esters by transesterification reaction [6,7]. The relevant signals chosen for integration are those of methoxy protons (singlet) and the α-carbonyl methylene protons (triplet). The simple equation used to quantify yield of transesterification is

$$C = 100 \times \frac{2A_{Me}}{3A_{CH_2}}$$

Where C, percentage conversion of triglycerides to corresponding methyl esters. A$_{Me}$, integration value of the methoxy protons of the methyl esters (the strong singlet) and A$_{CH2}$, integration value of α-methylene proton [8].

Table 4.6: ^{1}H NMR data (ppm) of oils

Oil	$-CH^a_2-CH^b-CH^c_2-$ Glyceridic (ppm)	α- CH_2 (ppm)	β- CH_2 (ppm)	Unsaturated olefinic -CH=CH- (ppm)
Rocket seed oil	^{a}4.15 (dd) ^{b}5.28 (m) ^{c}4.30 (dd)	2.33 (t)	1.62 (m)	5.35 (m)
Sesame oil	^{a}4.15 (dd) ^{b}5.29 (m) ^{c}4.30 (dd)	2.31 (t)	1.62 (m)	5.34 (m)
Linseed oil	^{a}4.12 (dd) ^{b}5.23 (m) ^{c}4.28 (dd)	2.28 (t)	1.59 (m)	5.31 (m)

Table 4.7: ^{1}H NMR data (ppm) of biodiesels

Biodiesel	CH_3O methoxy (ppm)	α- CH_2 (ppm)	β- CH_2 (ppm)	Unsaturated olefinic -CH=CH- (ppm)
RSOB	3.65 (s)	2.29 (t)	1.61 (m)	5.32 (m)
SOB	3.59 (s)	2.24 (t)	1.56 (m)	5.28 (m)
LSOB	3.63 (s)	2.27 (t)	1.60 (m)	5.33 (m)

The characteristics NMR shift values of protons for vegetable oils and methyl esters were observed. The methylene and the methine protons of the glyceridic sequence $-CH_2-CH-CH_2-$ can be observed at 4.15 (dd), 4.30 (dd) and 5.28 (m) ppm, respectively in rocket seed oil. The conversion of triglycerides into methyl esters (biodiesel) was confirmed by the disappearance of the resonance signals between 4.15-4.30, and the

emergence of the resonance signal at 3.65 ppm (strong singlet). Other peaks for ά-CH_2 (t) protons, β-CH_2 (m) protons, methylene protons of long aliphatic carbon chain (clusters of signals), olefinic protons (clusters of signals) and terminal methyl protons (t) are very similar in both oil and biodiesel. The percentage conversion of triglycerides to corresponding methyl esters in rocket seed oil determined by the above mention formula was 88.49%.

In sesame oil biodiesel, the characteristic peak of methoxy protons is observed at 3.59 ppm (singlet) and ά-CH_2 protons at 2.24 ppm (triplet). Other peaks were at 0.80 ppm of terminal methyl protons (t), a strong signal at 1.25 ppm related to methylene protons of carbon chain (cluster of signals), a signal at 1.54 ppm from β-methylene protons (m) and signals related to unsaturation at 1.95, 2.69 and 5.22 ppm assigned to allylic, bis-allylic and olefinic hydrogen, respectively. The percentage conversion of triglycerides to corresponding methyl esters in sesame oil was determined by the above mention formula was 96.66%.

In linseed oil the methylene and the methine protons of the glyceridic sequence –CH_2-CH-CH_2– can be observed in the range 4.12 (dd), 4.28 (dd) and 5.23 (m) ppm respectively. The conversion of triglycserides into methyl esters (biodiesel) was confirmed by the disappearance of the resonance signal between 4.12 (dd) and 4.28 (dd) and the emergence of the resonance signal at 3.63 ppm (strong singlet). Other peaks for ά-CH_2 protons, β-CH_2 protons, methylene protons of carbon chain, olefinic protons and terminal methyl protons are very similar in both oil and biodiesel. The percentage conversion of triglycerides to corresponding methyl esters in linseed oil determined by the above mention formula was 97%.

4.7.2 ^{13}C NMR Spectroscopy

The characteristic peaks of ester carbonyl (-COOR) and C-O (methoxy) are the distinct peaks for confirmation of methyl esters present in the biodiesel. The ^{13}C NMR of rocket seed oil, sesame oil and linseed oil data are given in the Table 4.8 and the representative spectra of rocket seed oil, linseed oil are shown in Figs 4.8- 4.10 respectively. The ^{13}C NMR of rocket seed oil biodiesel, sesame oil biodiesel and linseed oil biodiesel data are given in the Table 4.9 and the representative spectra are shown in Fig 4.8, 4.9 and 4.10. The methylene and methine carbons of the glyceridic sequence

–CH$_2$-CH-CH$_2$– can be observed in the range 62 and 68 ppm, respectively in rocket seed oil, sesame oil and linseed oil. Qualitative analysis indicates the conversion of triglycerides into methyl esters (biodiesel) by the disappearance of the resonance signal between 62 and 68 ppm and the emergence of the resonance signal at 51.3 ppm in RSOB, 51.2 ppm in SOB and 51.3 ppm in LSOB due to methoxy carbon. In vegetable oil and biodiesel containing saturated and unsaturated chains, the terminal methyl carbon resonance appear as a cluster of two or more signals in the range 14.0- 20.0 ppm. Each is indicative of a different environment for the methyl group. The signals for methylene carbons of long aliphatic chain [9-13], in the range of 22.5- 34.1 ppm are similar in both oil and biodiesel.

Table 4.8: ^{13}C NMR data (ppm) of oils

Oil	-COOR (triglyceridic)	Olefinic carbon C=C	Glyceridic –CH$_2$	Glyceridic –CH
Rocket seed oil	172.7-173.2	127.1—131.9	62.0	68.8
Sesame oil	172.8-173.2	127.8-130.1	62.0	68.8
Linseed oil	172.6-173.0	127.0-131.8	62.0	68.8

Table 4.9: ^{13}C NMR data (ppm) of biodiesels

Biodiesel	-COOR (methyl ester)	CH$_3$O (methoxy)	Olefinic carbon C=C
RSOB	174.2	51.3	127.0-131.8
SOB	174.0	51.2	127.8-129.9
LSOB	174.1	51.3	127.0-131.8

4.8 GC-MS Spectroscopy

GC-MS is used to study the chemical composition of the biodiesel products. FAMEs are suitable for separation, identification, quantification and analysis by GC. Different FAMEs are separarted at different retention time. Different peaks are obtained in the GC spectrum. The GC spectrums of RSOB, SOB and LSOB, are shown in Fig. 4.11- 4.13 respectively. Each peak corresponds to a fatty acid methyl ester which was identified by library match software. The identified FAMEs in RSOB, SOB and LSOB, with their retention time are shown in Table 4.10- 4.12, respectively. The GC was fitted with non-polar column in which unsaturated FAMEs elute in front of saturated ones and cis-isomer elute before their trans-isomer analogues. MS attached with GC is a powerful technique for diagnostic fragmentation of saturated and unsaturated FAMEs. The chain length, number of double bonds and double bond positions are determined by mass spectrum. The mass spectrum was achieved by electron impact ion source. There were two types of FAMEs observed in biodiesel, saturated FAMEs and unsaturated FAMEs.

4.8.1 Saturated FAMEs

In RSOB, SOB and LSOB, five, three and three saturated FAMEs, respectively were identified in GC-MS. The electron impact spectra of saturated FAMEs were very similar, having characteristics peaks of fragment ions. The molecular ion peak is usually weak. Each FAME was separated out at specific retention time by gas chromatography. So the retention time and mass fragmentation pattern help to identify and verify the FAMEs. The base peak in all saturated FAMEs is observed at m/z 74 which is a product of well-known McLafferty rearrangement process [14], a peak $[M-31]^+$ due to α-cleavage (loss of methoxy group) and $[M-43]^+$ due to rearrangement of the chain and one hydrogen atom, followed by expulsion of a propyl radical (carbon 2 to 4). Other characteristic ions include at m/z 87, the first member of the carbomethoxy ion series due to β-cleavage $[CH_3OOC(CH_2)_n]^+$, where n = 2, 3, 4, ..., m/z = 87, 101, 115, 129, 143..., with difference of 14 a.m.u. and a hydrocarbon series of ions (alkyl series, C_nH_{2n+1}) that are abundant in the low-mass region. Thus β-cleavage and alkyl series support the identification of saturated FAMEs. The fragmentation pattern of saturated fatty acid methyl esters (methyl hexadecanoate (C16:0) is shown in Fig. 4.14. The mass spectrum

of methyl docosanoate (C22:0) from rocket seed oil biodiesel and mass spectrum of methyl hexadecanoate (C16:0) from sesame oil biodiesel are shown in Fig. 4.15 and 4.16 respectively.

4.8.2 Unsaturated FAMEs

In RSOB, SOB and LSOB, five, three and three unsaturated FAMEs were identified in GC-MS. The retention time by GC and mass fragmentation pattern by MS help to identify the **monounsaturated** FAMEs. In RSOB, all five unsaturated FAMEs were monounsaturated while in SOB and LSOB, two FAMEs in each were monounsaturated. They have very similar fragmentation pattern having characteristic peaks at m/z 55 (base peak), $[M-32]^+$ due to loss of methanol (methoxy group plus hydrogen atom) and $[M-74]^+$ due to loss of McLafferty ion. These three characteristic peaks help to identify monounsaturated FAMEs. Other characteristic ion include hydrocarbon ions $[C_nH_{2n-1}]^+$, $[C_nH_{2n}]^+$ and $[M-88]^+$, $[M-102]^+$, $[M-116]^+$ etc. due to loss of a fragment containing the carbonyl group by cleavage between carbon 3 and 4, 4 and 5, 5 and 6 with addition of a rearranged hydrogen atoms, the mass spectrum of methyl 9-octadecenoate (C18:1) from rocket seed oil biodiesel (RSOB) is shown in Fig. 4.17. The identified unsaturated FAMEs in rocket seed oil biodiesel (RSOB) along with retention time and characteristics ions at various m/z values are shown in Table 4.13 and 4.14.

In SOB, one diunsaturated FAME was identified in GC-MS. Diunsaturated FAMEs have a very similar pattern of fragmentation with a characteristic base peak at m/z 67, an ion $[M-31]^+$ due to loss of methoxyl group and an ion $[M-74]^+$ due to loss of McLafferty ion. The mass spectrum of methyl 9, 12 -octadecadienoate (C18:2) from sesame oil biodiesel is shown in Fig. 4.18.

In LSOB, a methyl 9, 12, 15- octadecatrienoate (C18:3) was identified and its mass spectrum is shown in Fig. 4.19. In this methylene-interrupted trienes, there is usually a distinctive moleculer ion together with a small ion $[M-31/32]^+$ for loss of the elements of a methoxyl group (plus a hydrogen atom). The McLafferty ion (m/z = 74) is also observed. The base peak consists of hydrocarbon ion of formula $[C_nH_{2n-5}]^+$ at m/z = 79.

Table 4.10: FAMEs composition of RSOB

Peak no.	RT(min^{-1})	Identified compounds and their formulae:
1.	11.19	methyl 9-hexadecenoate (C16:1) $CH_3OCO(CH_2)_7CH=CH-(CH_2)_5CH_3$
2.	11.40	14-methyl pentadecanoate(C15:0) $CH_3OCO(CH_2)_{12}CH(CH_3)_2$
3.	13.15	methyl 9-octadecanoate (C18:1) $CH_3OCO(CH_2)_7CH=CH(CH_2)_7CH_3$
4.	13.33	methyl octadecanoate(C18:0) $CH_3OCO(CH_2)_{16}CH_3$
5.	14.93	methyl 11-eicosenoate (C20:1) $CH_3OCO(CH_2)_9 CH=CH-(CH_2)_7CH_3$
6.	15.10	methyl eicosanoate(C20:0) $CH_3OCO(CH_2)_{18} CH_3$
7	16.60	methyl 13-docosenoate (C22:1) $CH_3OCO(CH_2)_{11}CH=CH-(CH_2)_7CH_3$
8.	16.77	methyl docosanoate(C22:0) $CH_3OCO(CH_2)_{20}CH_3$
9.	18.12	methyl 15-tetracosenoate (C24:1) $CH_3OCO(CH_2)_{13}CH=CH-(CH_2)_7CH_3$
10	18.27	methyl tetracosanoate (C24:0) $CH_3OCO(CH_2)_{22}CH_3$

Table 4.11: FAMEs composition of SOB

Peak No.	RT(min)	Identified compounds and their formulae
1.	11.44	methyl hexadecanoate (C16 : 0) $CH_3OCO(CH_2)_{14}CH_3$
2.	13.14	methyl 9,12-Octadecadienoate (C18 : 2) $CH_3OCO(CH_2)_7CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$
3.	13.38	methyl octadecanoate (C18 : 0) $CH_3OCO(CH_2)_{16}CH_3$
4.	14.93	methyl 11-eicosenoate (20:1) $CH_3OCO(CH_2)_9\ CH=CH-(CH_2)_7CH_3$
5.	15.13	methyl eicosanoate (C20 : 0) $CH_3OCO(CH_2)_{18}\ CH_3$
6.	16.60	methyl 13-docosenoat (22:1) $CH_3OCO(CH_2)_{11}CH=CH-(CH_2)_7CH_3$

Table 4.12: FAMEs composition of LSOB

Peak No.	RT (min^{-1})	Identified compounds and their formulae
1.	11.43	methyl hexadecanoate (C16:0) $CH_3OCO(CH_2)_{14}CH_3$
2.	13.19	methyl 9,12,15- octadecatrienoate (C18:3) $CH_3OCO(CH_2)_7CH=CH-CH_2-CH=CH-$ $CH_2-CH=CH-CH_2-CH_3$
3.	13.38	methyl octadecanoate (C18:0) $CH_3OCO(CH_2)_{16}CH_3$
4.	14.92	methyl 11-eicosenoate (C20:1) $CH_3OCO(CH_2)_9CH=CH-(CH_2)_7CH_3$
5.	15.11	methyl eicosanoate (C20:0) $CH_3OCO(CH_2)_{18}CH_3$
6.	16.59	methyl 13-docosenoate (C22:1) $CH_3OCO(CH_2)_{11}CH=CH-(CH_2)_7CH_3$

Table 4.13: Fragmentation pattern of saturated FAMEs in RSOB

RT (min^{-1})	FAMEs	[M]$^{+\cdot}$	[(McL]$^{+\cdot}$	[M-31]$^+$	[M-43]$^+$	β-cleavage $[(CH_2)_nCOOCH_3]^+$	Alkyl series C-C cleavage $(C_nH_{2n+1})^+$
11.40	methyl 14- methyl pentadecanoate (C15:0) (C15:0)	270	74	239	227	87,101,115,129,143	15, 29, 43…
13.33	methyl octadecanoate (C18:0)	298	74	267	255	87,101,115,129,143	15, 29, 43…
15.10	methyl eicosanoate (C20:0)	326	74	295	283	87,101,115,129,143	15, 29, 43…
16.77	methyl docosanoate (C22:0)	354	74	323	311	87,101,115,129,143	15, 29, 43…
18.27	methyl tetracosanoate (C24:0)	382	74	351	339	87,101,115,129,143	15, 29, 43…

Table 4.14: Fragmentation pattern of monounsaturated FAMEs in RSOB

RT (min⁻¹)	FAMEs	$[M]^+$	$[M-32]^+$	$[M-74]^+$	$[C_nH_{2n-1}]^+$	$[M-88]^+$	$[M-102]^+$	$[M-116]^+$
11.19	methyl 9- hexadecenoate (C16:1)	268	236	194	55	180	166	152
13.15	methyl 9-octadecenoate (C18:1)	296	264	222	55	208	164	180
14.93	methyl 11-eicosenoate (C20:1)	324	292	250	55	236	222	208
16.60	methyl 13-docosenoate (C22:1)	352	320	278	55	264	250	236
18.12	methyl 15-tetracosenoate (C24:1)	380	348	306	55	292	278	264
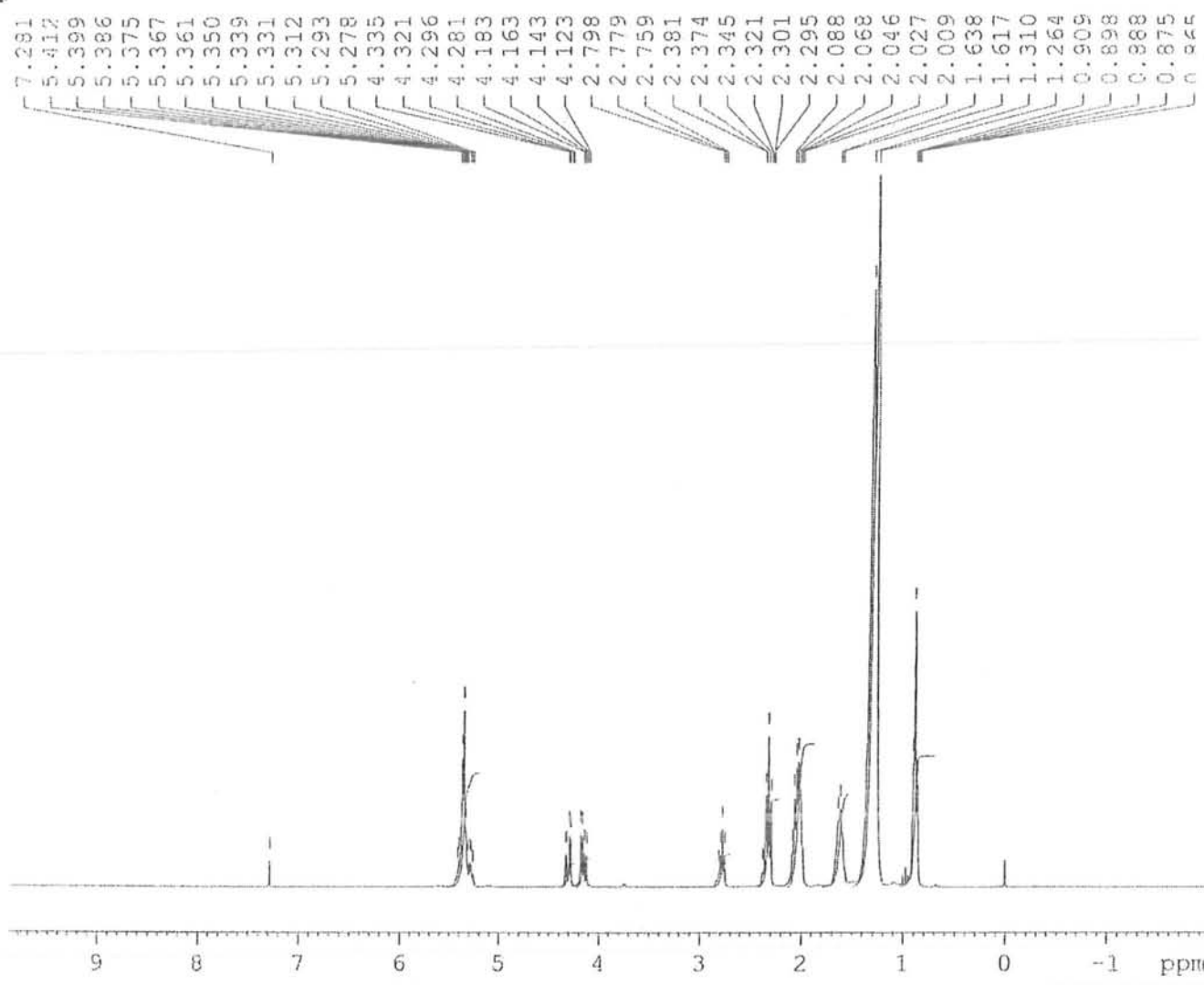
Fig. 4.1. ¹H NMR spectrum of triglycerides in rocket seed oil
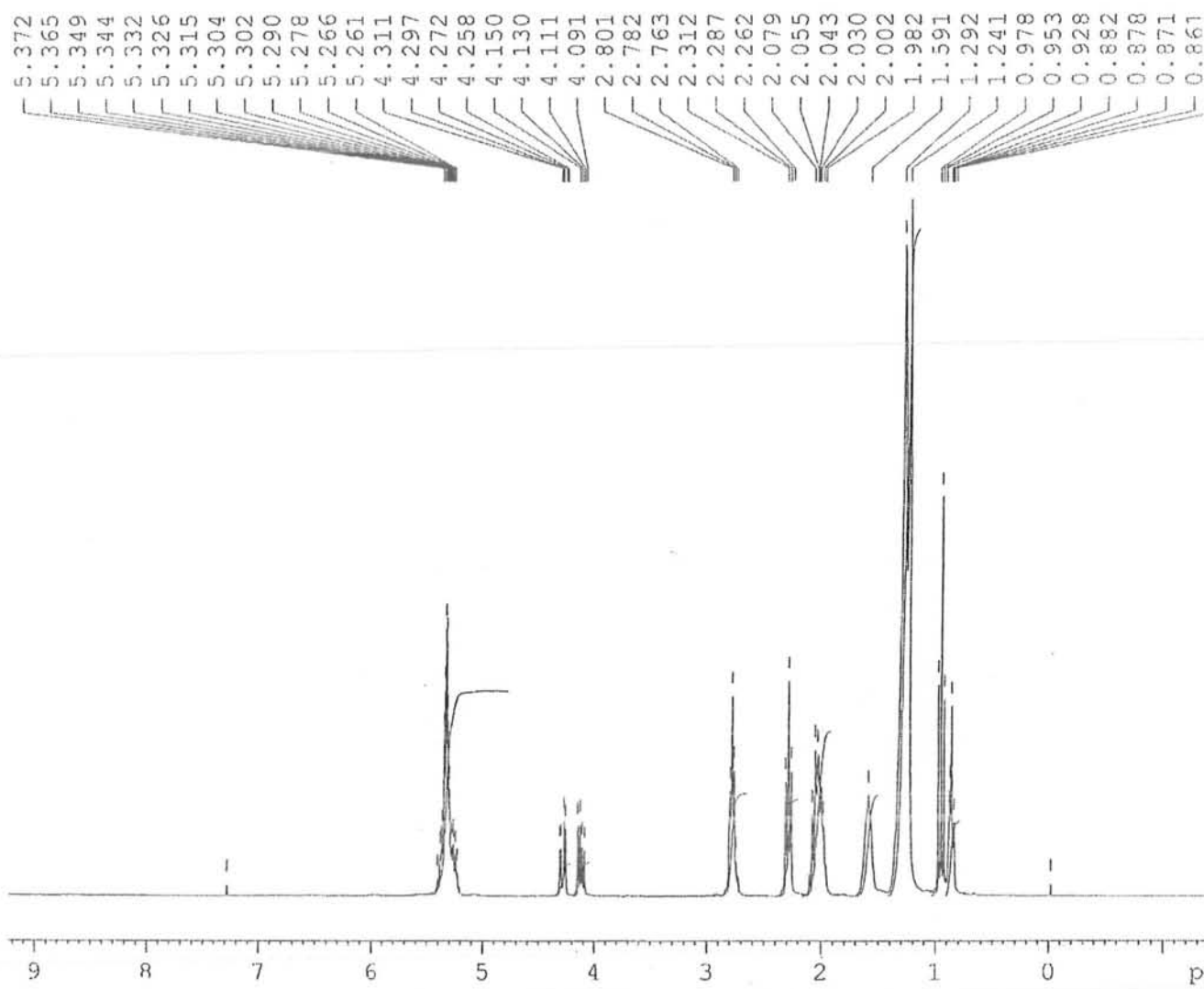
Fig. 4.2. ^{1}H NMR spectrum of triglycerides in linseed oil
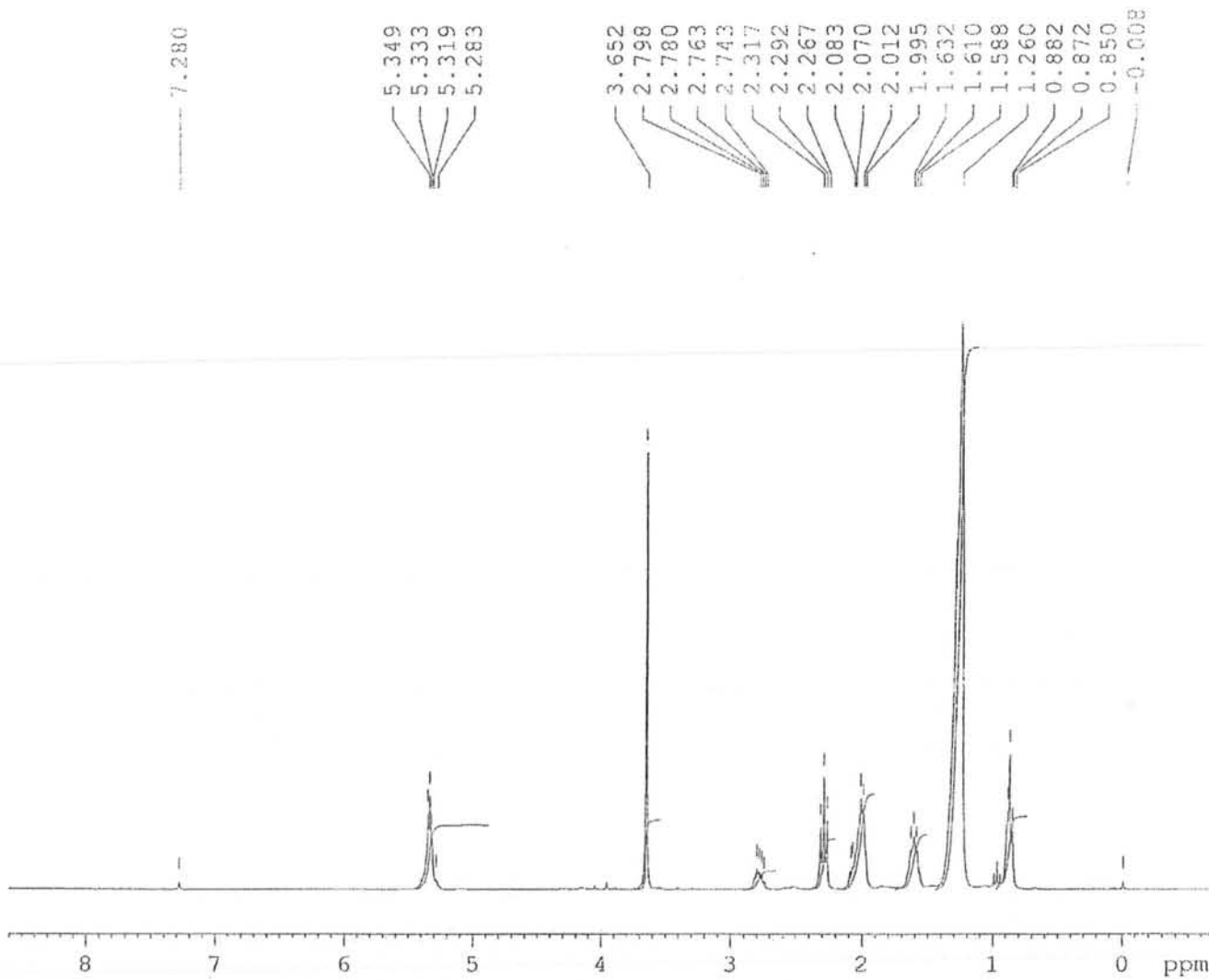
Fig. 4.3: ^{1}H NMR spectrum of methyl esters in RSOB

Fig. 4.4: ¹H NMR spectrum of methyl esters in SOB

7.279

5.341
5.333
5.329
5.318
5.300
5.282
5.272
5.264
5.246
5.227
5.223

3.599
2.736
2.718
2.698
2.268
2.244
2.218
2.032
2.010
1.988
1.970
1.952
1.592
1.569
1.546
1.263
1.257
1.212
0.864
0.852
0.842
0.832
0.819
0.809

45
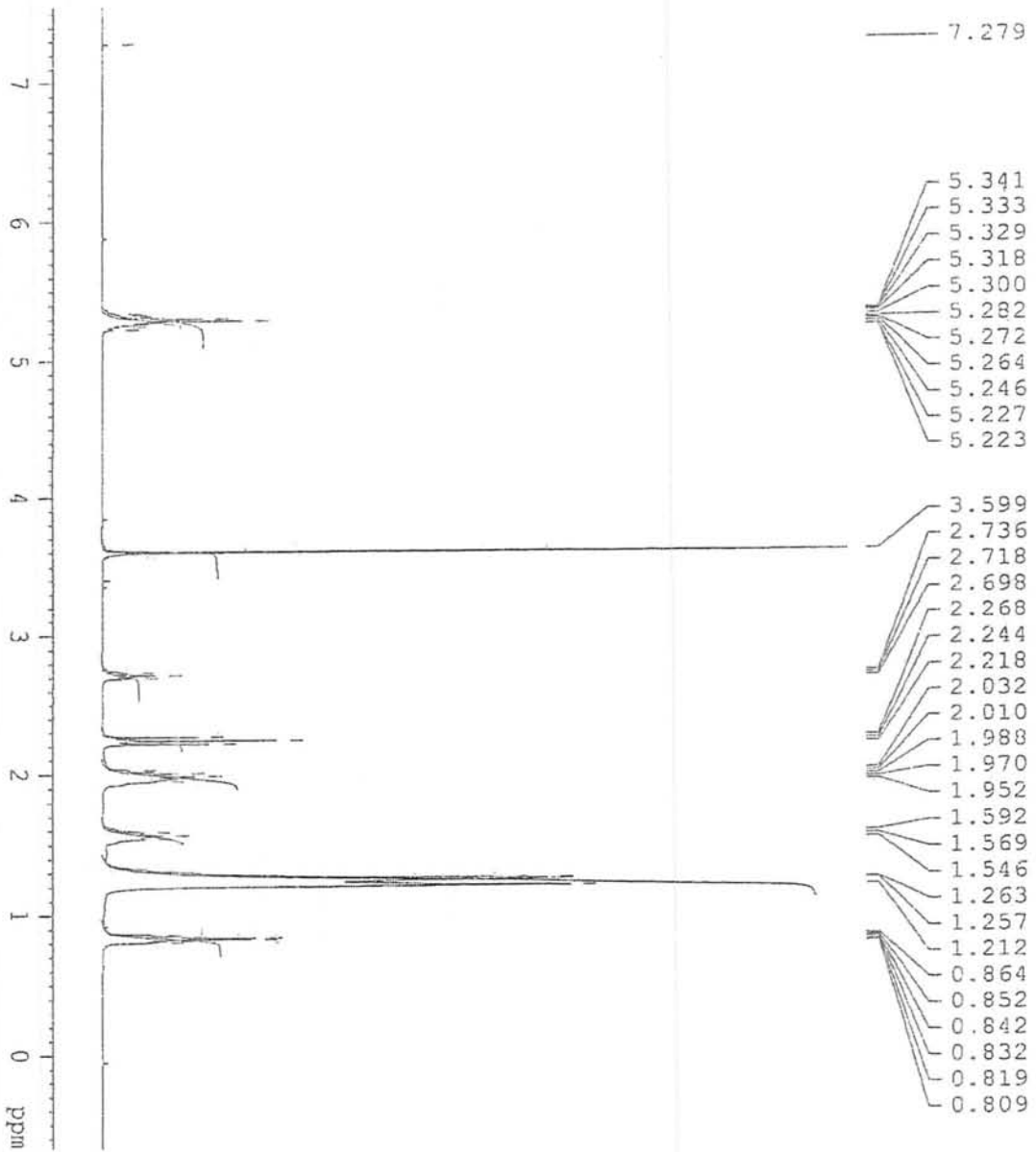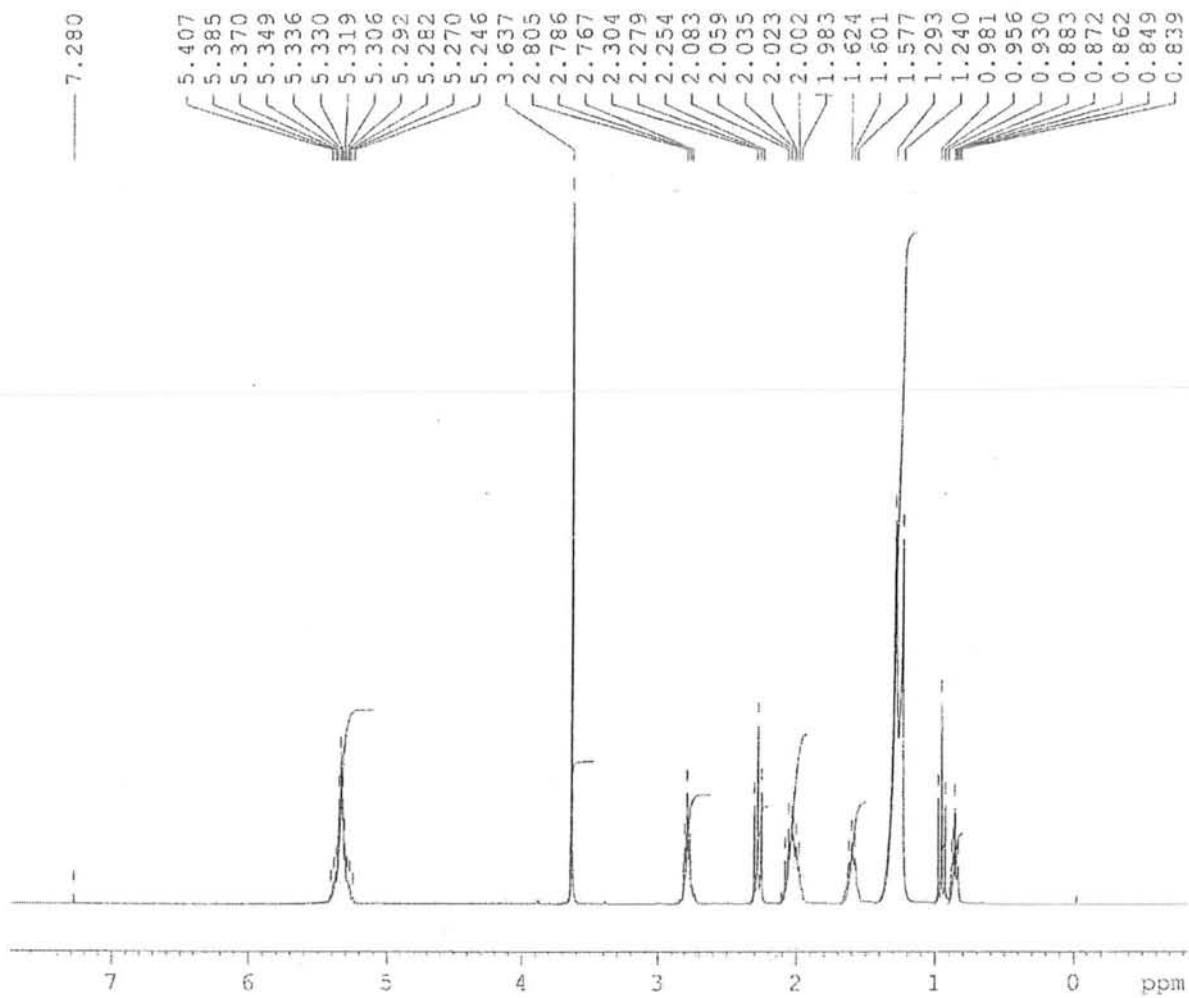
Fig. 4.5: ^{1}H NMR spectrum of methyl esters in LSOB
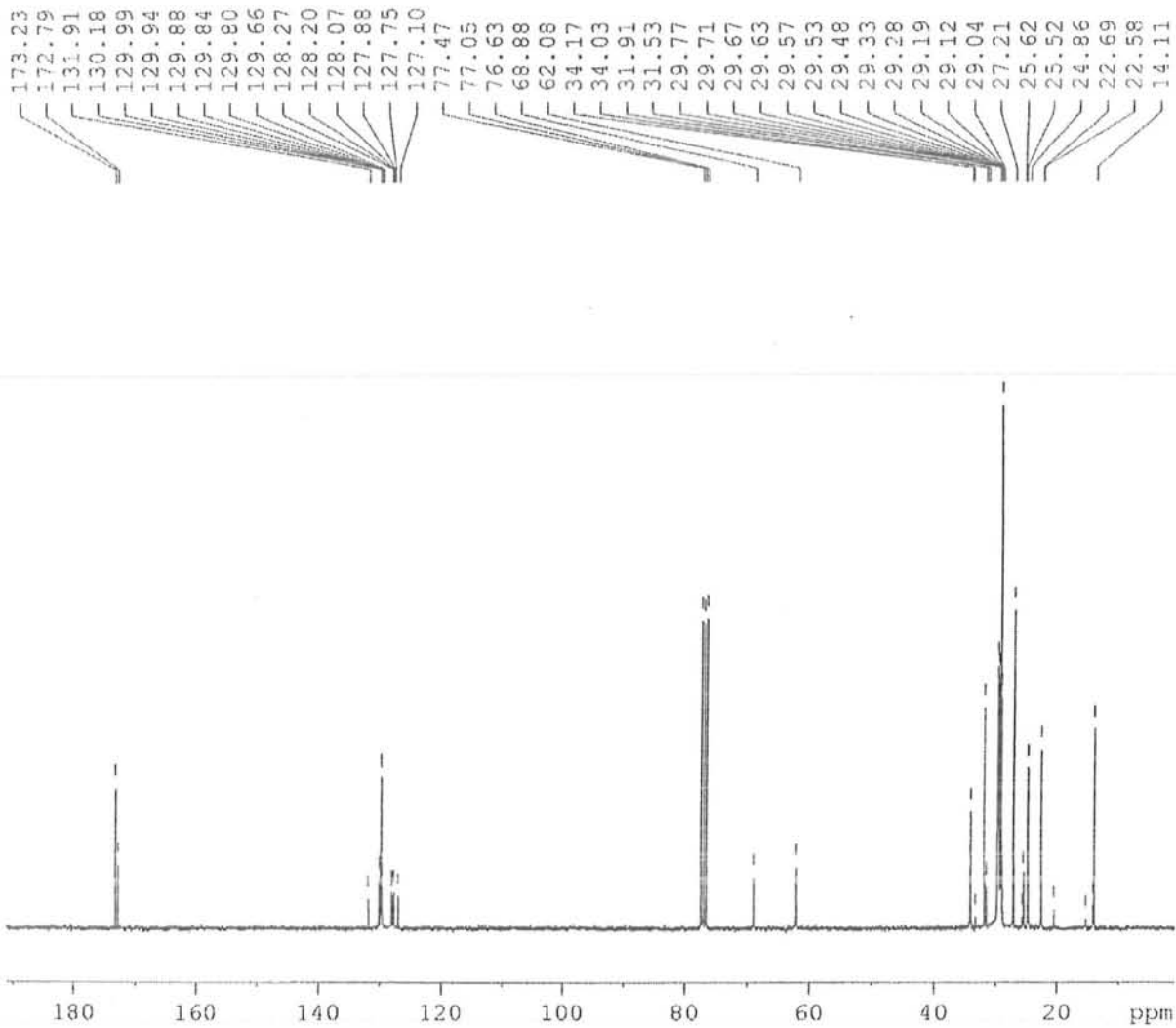
Fig. 4.6 ^{13}C NMR spectrum of rocket seed oil
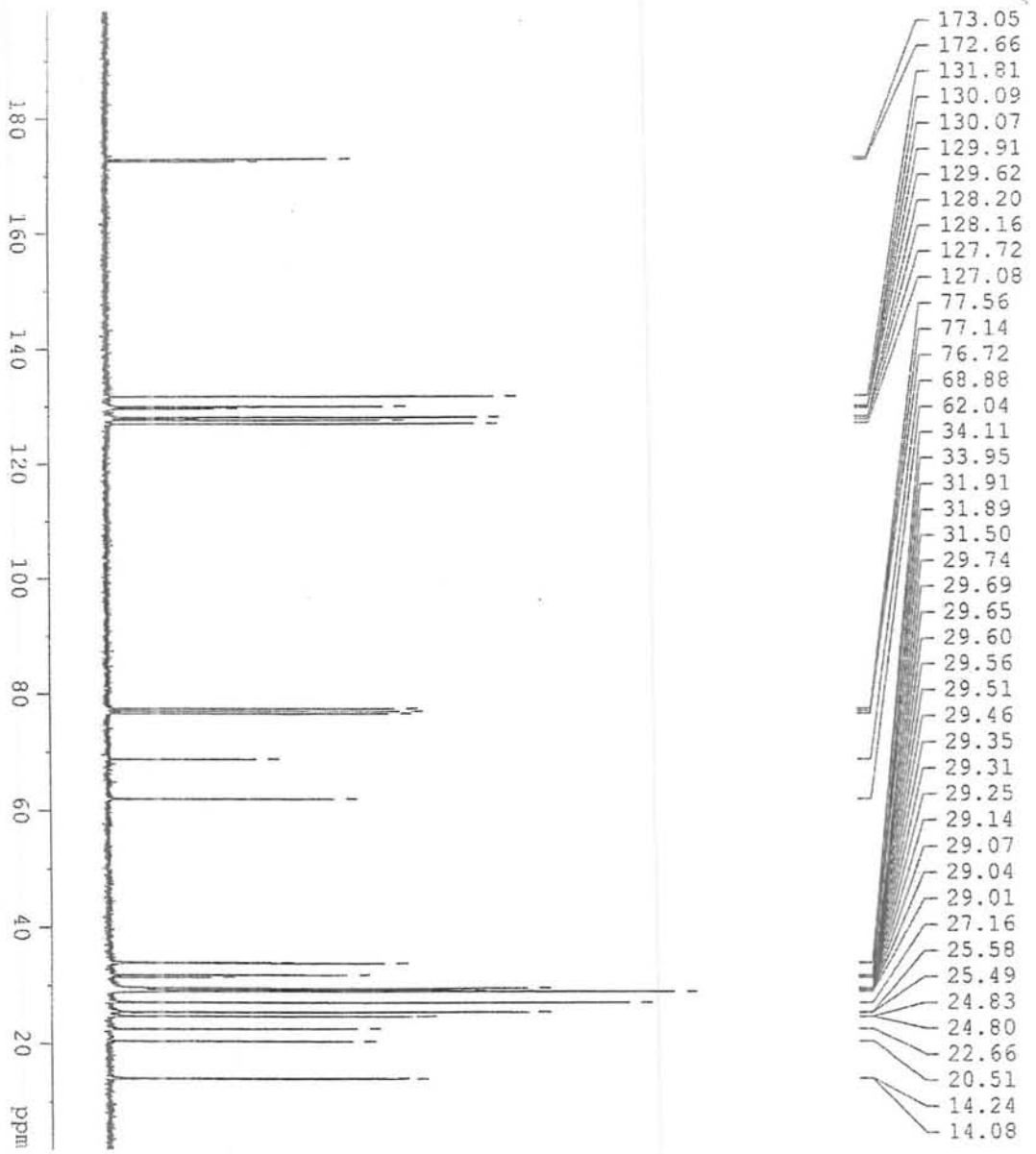
Fig. 4.7 ^{13}C NMR spectrum of linseed oil

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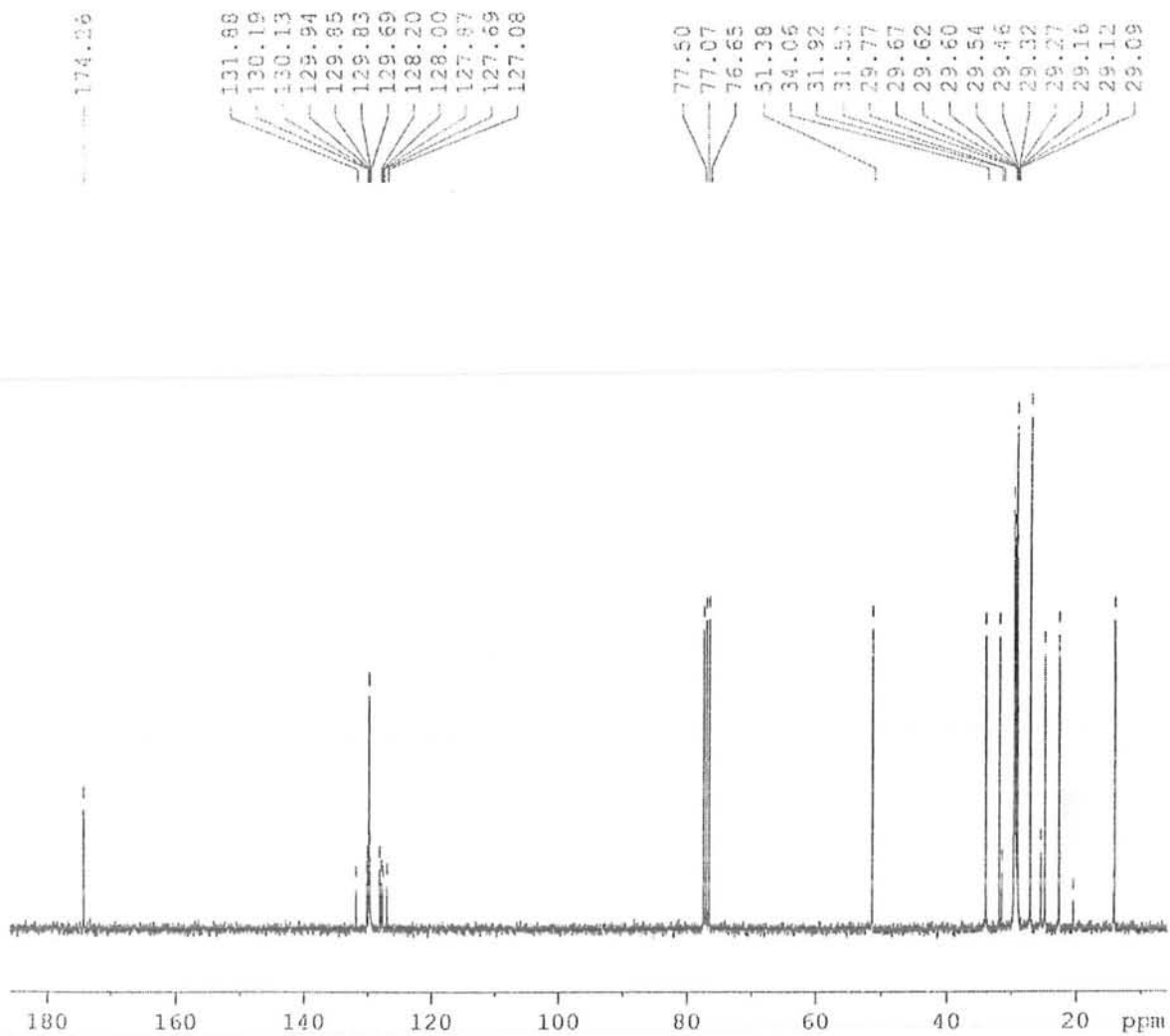
Fig. 4.8: ^{13}C NMR spectrum of methyl esters in RSOB
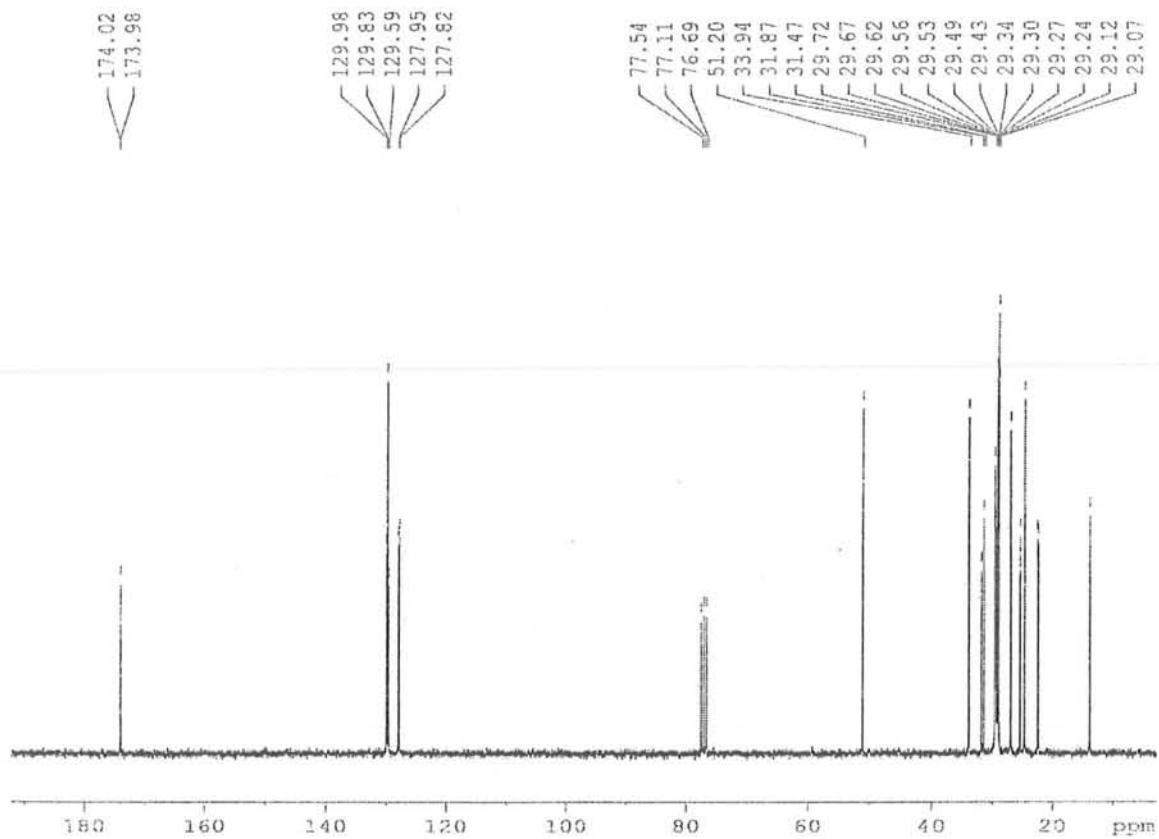
Fig. 4.9: ^{13}C NMR spectrum of methyl esters in SOB
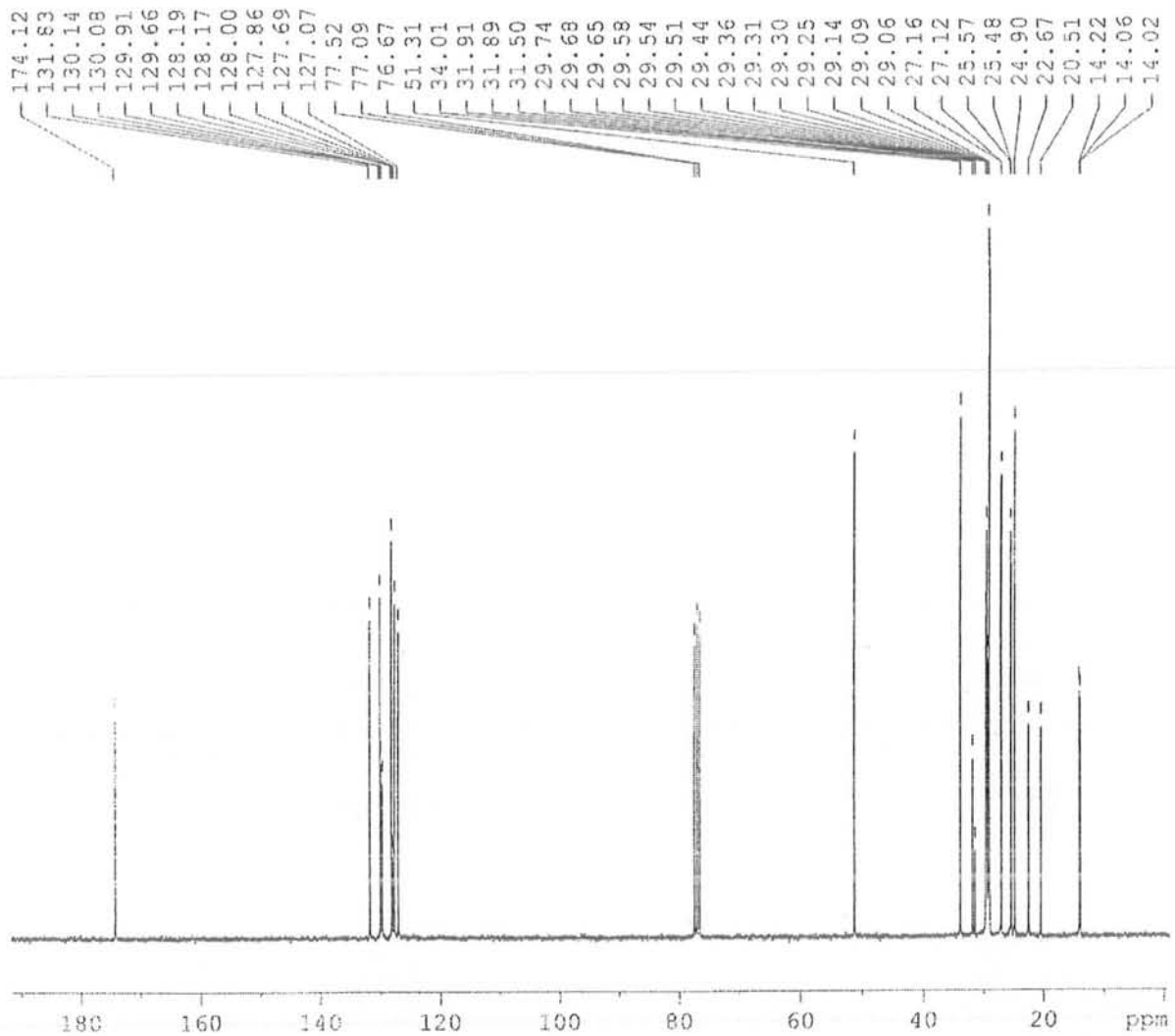
Fig. 4.10: ^{13}C NMR spectrum of methyl esters in LSOB
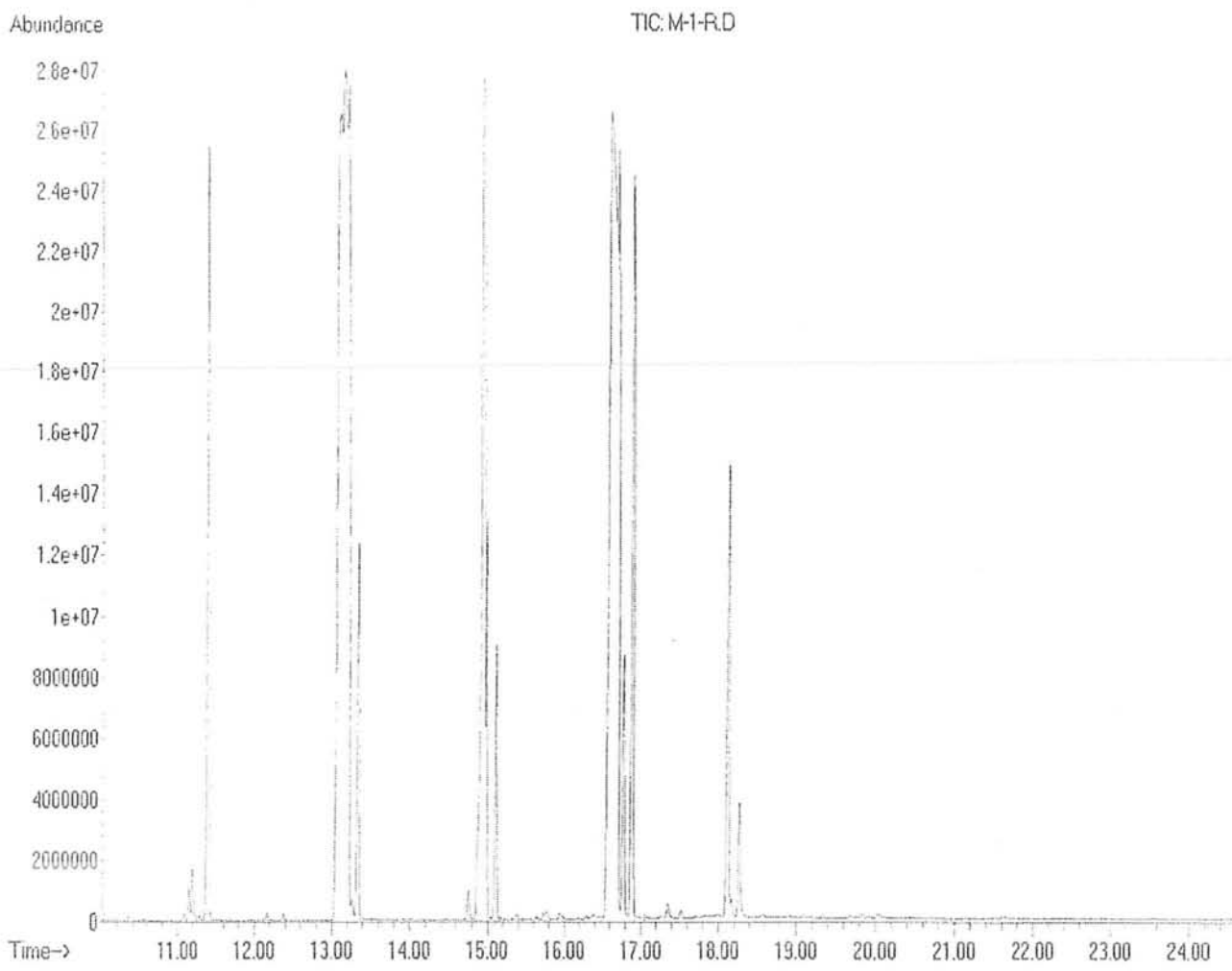
Fig. 4.11: Gas chromatogram of RSOB showing composition of fatty acid
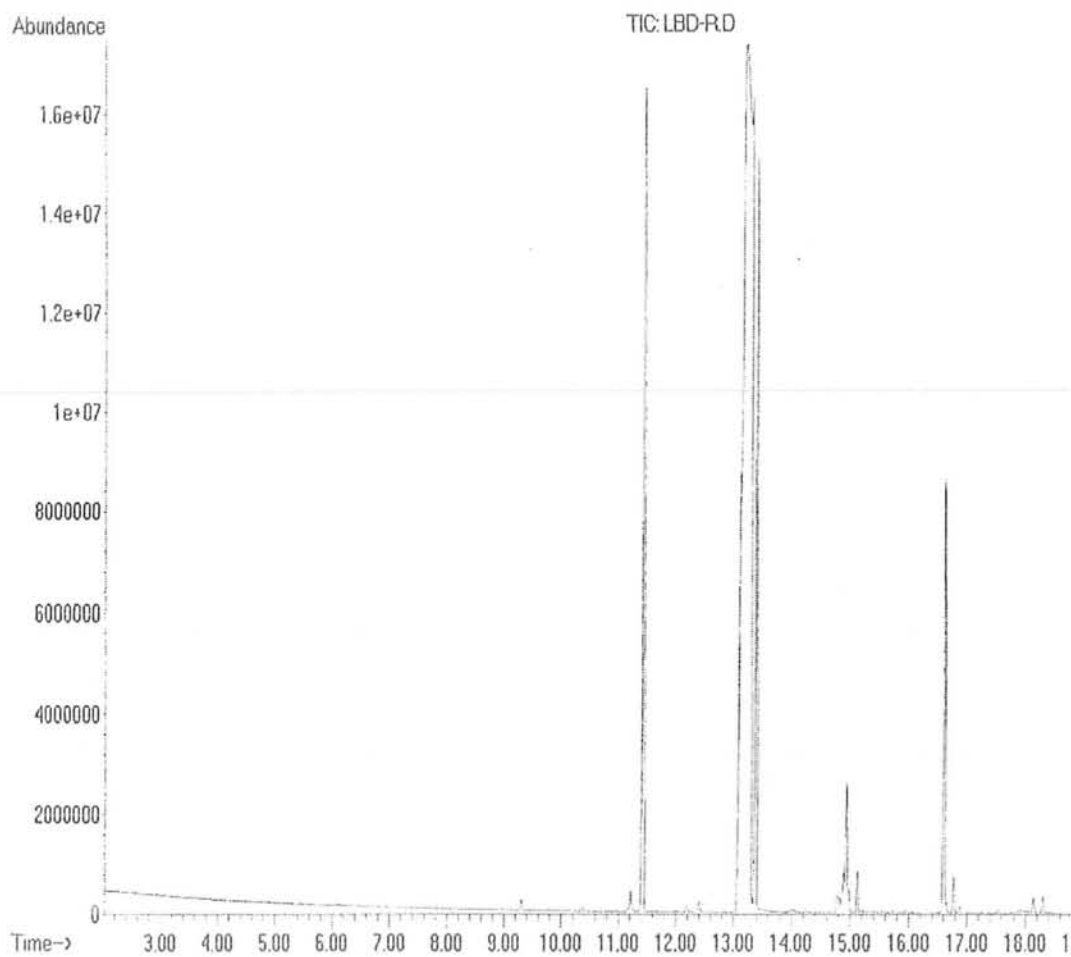methyl esters
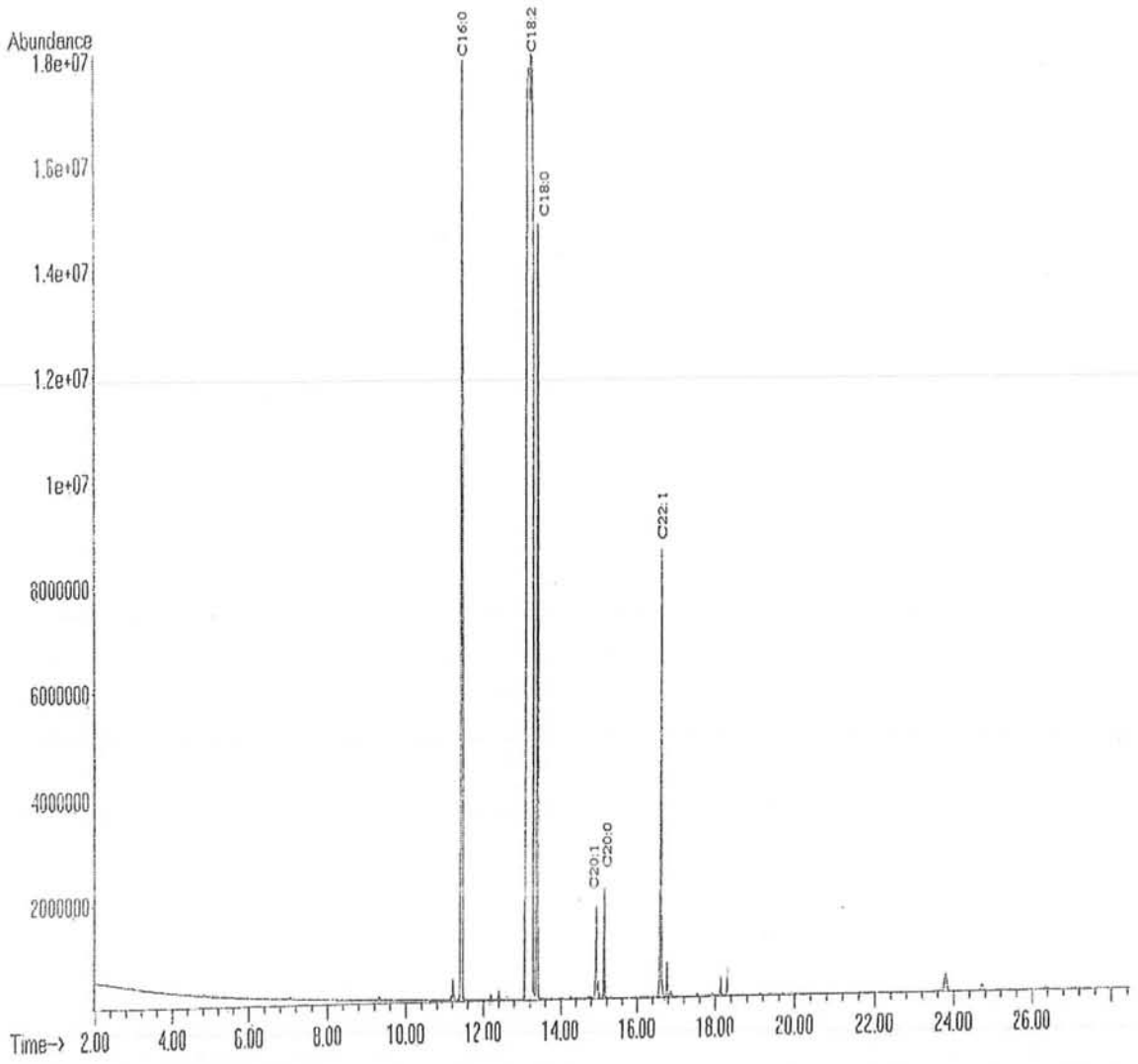
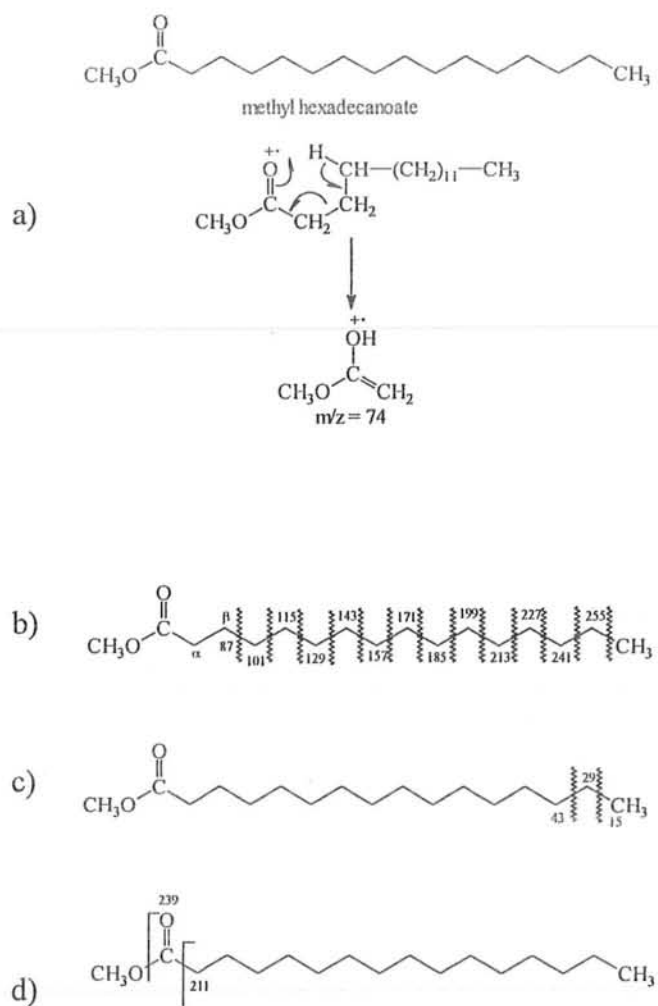Fig. 4.12: Gas chromatogram of SOB showing composition of fatty acid methyl esters

Fig. 4.13: Gas chromatogram of LSOB showing composition of fatty acid methyl esters

Fig. 4.14: Mass fragmentation pattern of saturated fatty acid methyl esters (methyl hexadecanoate)
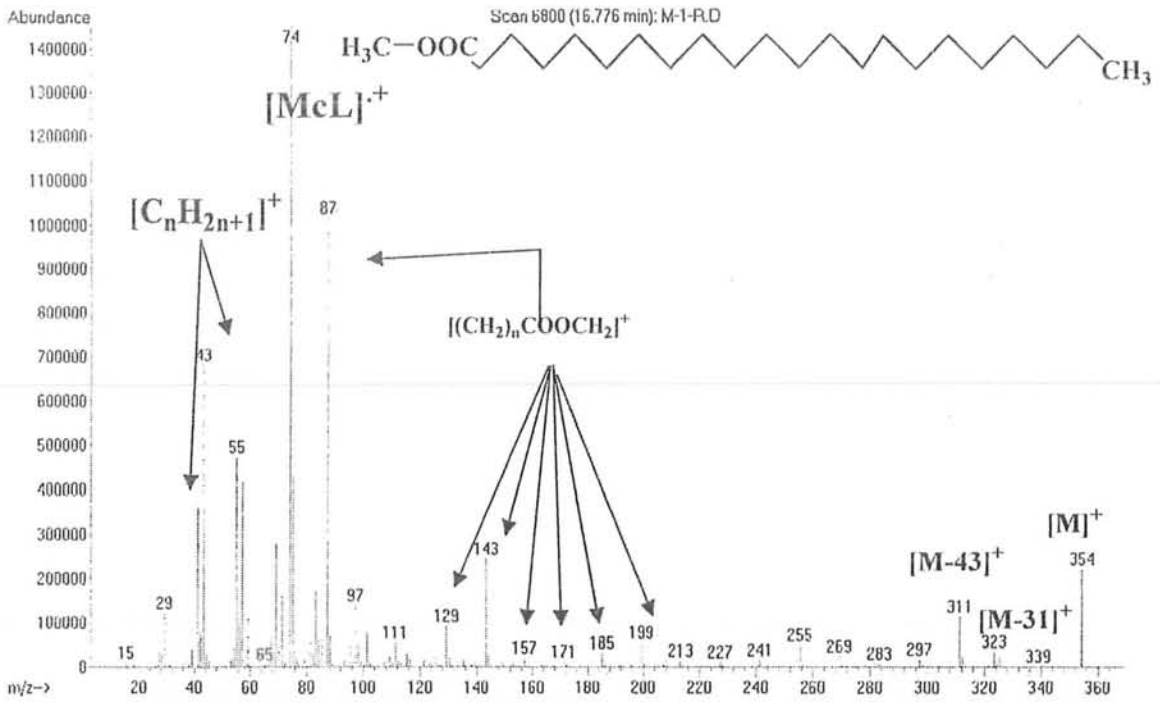
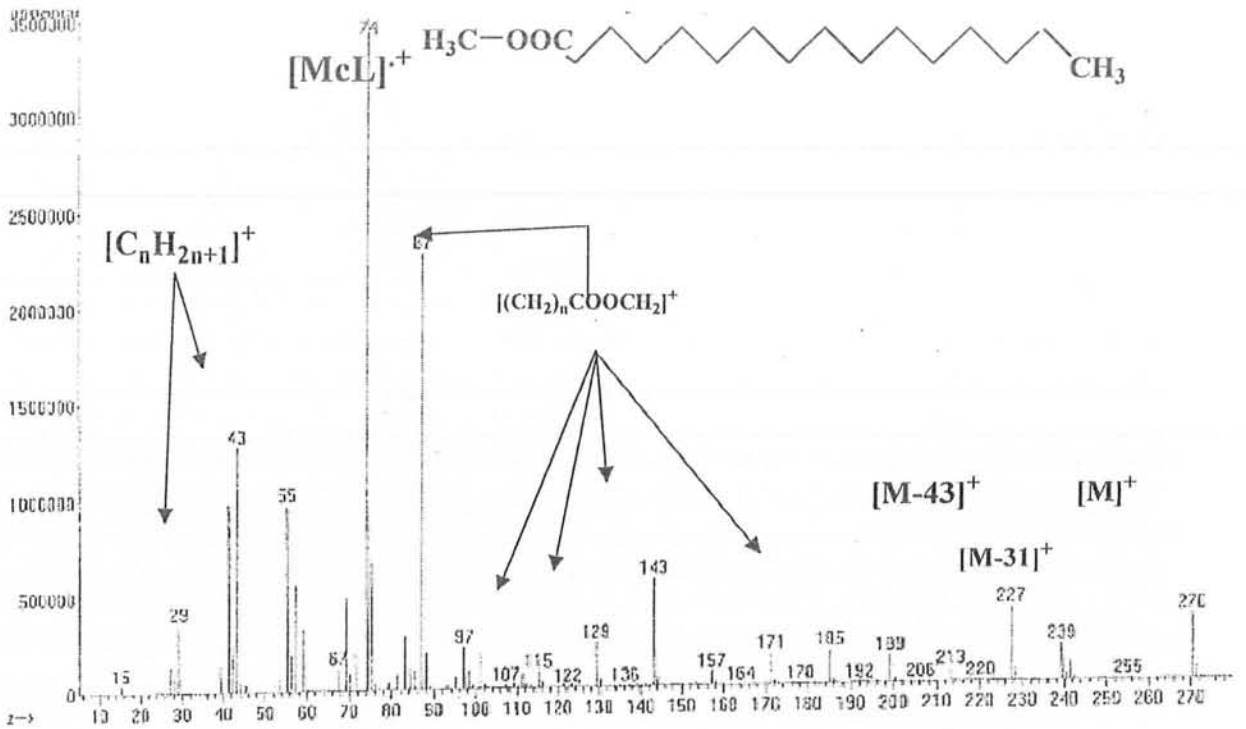Fig. 4.15: Mass spectrum of methyl docosanoate (C22:0) from RSOB

Fig. 4.16 Mass spectrum of methyl hexadecanoate (C16:0) from SOB
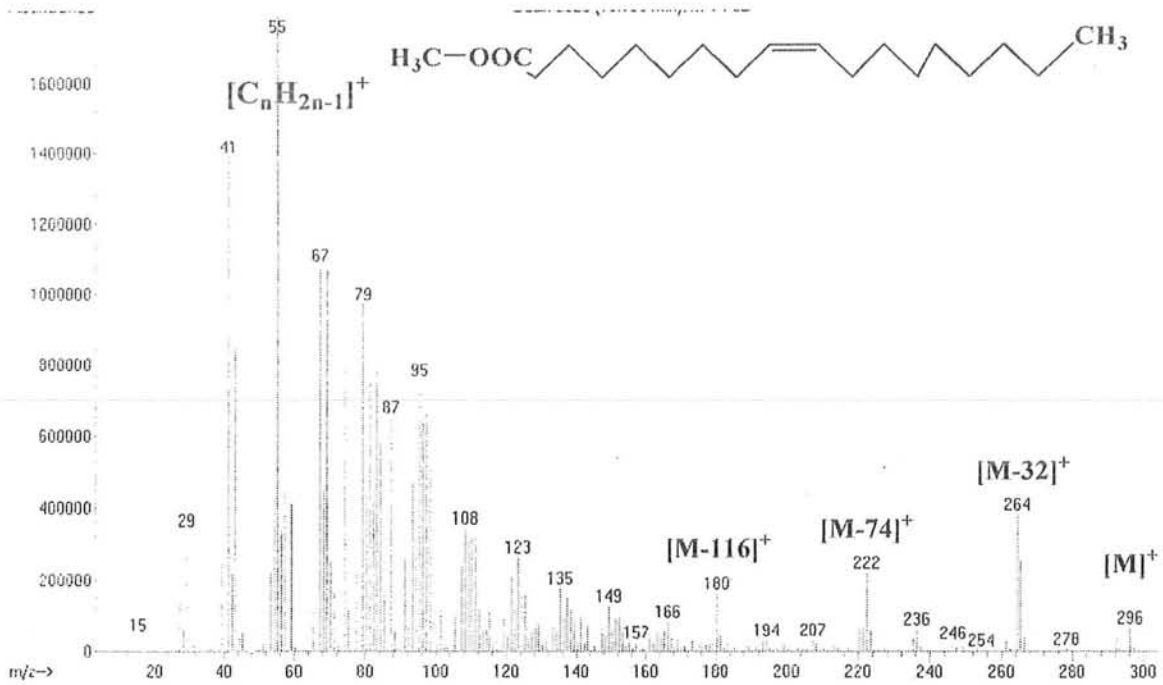
56

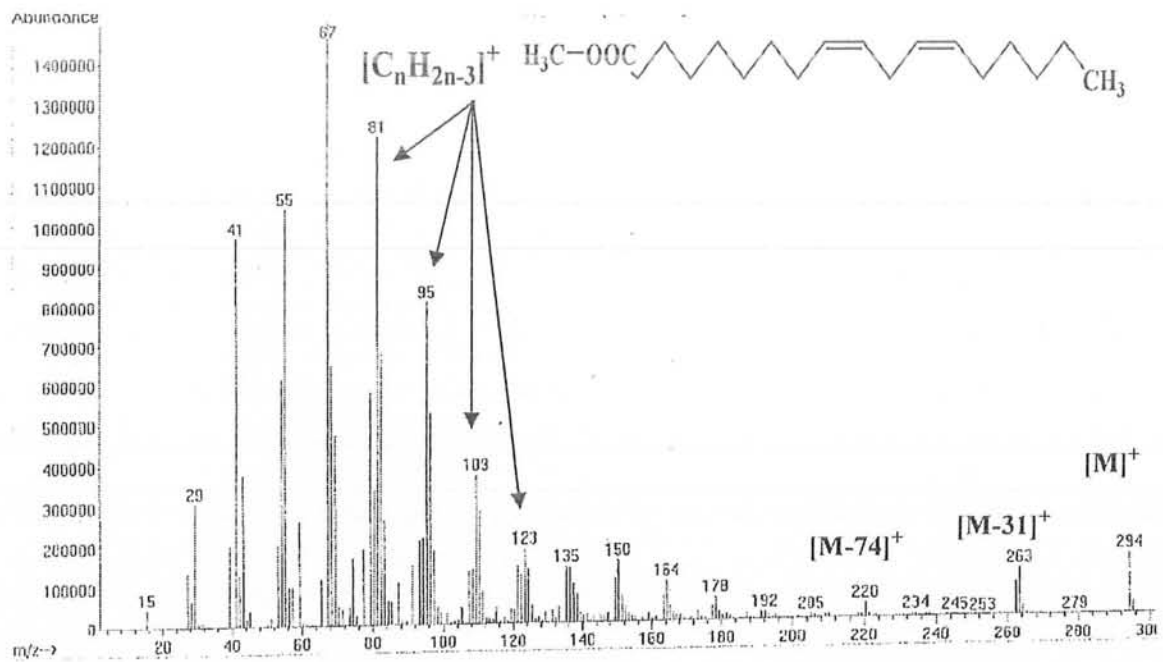Fig. 4.17: Mass spectrum of methyl 9- octadecenoate (C18:1) from RSOB

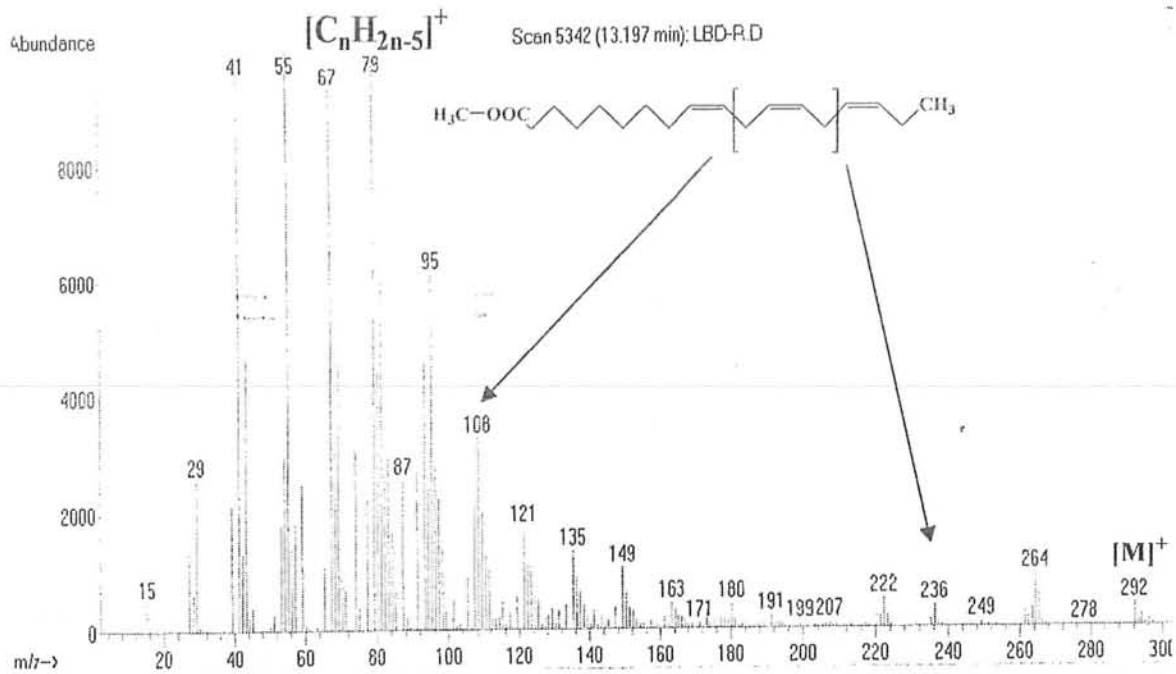Fig. 4.18: Mass spectrum of methyl 9, 12- octadecadienoate (C18:2) from SOB

Fig. 4.19 Mass spectrum of methyl 9, 12,15- octadecatrienoate (C18:3) from
LSOB

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CONCLUSIONS

- Biodiesel was synthesized from rocket seed oil, linseed oil and sesame oil by base catalyzed transesterification with methanol.

- The maximum yield of biodiesel was achieved through methanolysis of crude oil of these species at 1: 6 molar ratio of oil and methanol at 60 °C.

- The physical parameters (dynamic viscosity, kinematic viscosity, acid number, density) of biodiesel were determined and found comparable to ASTM standards.

- The fuel properties of biodiesel such as cetane number, cloud point, pour point and flash point were determined and found comparable to ASTM standards.

- FT-IR and NMR (^{1}H and ^{13}C) analysis of oil and biodiesel were performed which confirmed the synthesis of biodiesel. The conversion of triglycerides into methyl esters (biodiesel) was confirmed by the disappearance of the resonance signal of methylene and the methine protons of the glyceridic sequence $-CH_2-CH-CH_2-$ and the emergence of the resonance signal of methoxy protons (strong singlet).

- The chemical composition (FAMEs) of RSOB, SOB and LSOB were determined by GC-MS analyses. The identified FAMEs were verified by retention time data and mass fragmentation pattern.