Nano Catalytical Conversion of Used Oil into Biofuels

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IN THE NAME OF ALLAH,

MOST BENEFICIENT,

THE MOST MERCIFUL

Dedicated To
My Parents,
Siblings
and Friends

(Acceptance by the Viva Voce Committee)

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02,01,2012

DECLARATION

I hereby declare that the work present in the following thesis is my own effort, except where otherwise acknowledged and that the thesis is my own composition. No part of the thesis has been previously presented for any other degree.

Date 02-01-2012

Maria Saeed

FORWARDING SHEET

The thesis entitled Nano Catalytical Conversion of Used Oil into Biofuels submitted by Maria Saeed in partial fulfillment of MS in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow her to submit this thesis, for further processes per IIU rules and regulations.

Dr. Maliha Asma

Abstract

The production of biodiesel from waste cooking oil comparable in quality to that of virgin vegetable oil offers a triplet-facet solution: economical, environmental and waste management. There is an imperative need to investigate alternative and innovative production processes from both economic and environmental view points and. This study highlights the new and innovative nano technology overcoming the limitations of conventional techniques .The novel cobalt, nickel, copper-nickel and copper cerium oxide nano particles were synthesized and characterized by XRD, SEM, EDX and BET. These nano particles were further used as catalysts for the conversion of waste cooking oil into biodiesel. Experiments were conducted by using these catalysts at different operational conditions. The biodiesel yield along with confirmation of biodiesel was detected by NMR, FTIR and GC/MS techniques. At optimum condition the biodiesel yield of 96% was achieved. For supporting these nano catalysts comparative studies were carried out using conventional base catalyst at established temperature and molar ratios. From the operational established parameters of conventional methodology the yield of biodiesel was 78%.

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All praise and glory to Almighty **Allah** who is the ultimate creator of this universe: from particles to the stars, who blessed us with the ability to think and an eager heart to explore this whole universe. Countless salutations upon the **Holy Prophet Hazrat Muhammad (S.A.W)** the source of knowledge and blessings for entire mankind.

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Maria Saeed

List of Abbreviations

GHG	Green House Gases
WHO	World Health Organization
mb/d	Mobilidium per Demand
WCO	Waste Cooking Oil
OECD	Organization for Economic Co-operation and Development
FFA	Free Fatty Acid
v/v	volume/volume Weight Percentage
°C	Centigrade
FAME	Fatty Acid Methyl Esters
ASTM	American Society for Testing of Material
XRD	X-ray Diffraction Technique
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray Analysis
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectroscopy
GC/MS	Gas Chromatography/ Mass Spectrometry
BET	Brauner Emitt Teller
WCOME	Waste Cooking Oil Methyl Esters

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CHAPTER #1

INTRODUCTION

1 INTRODUCTION

In the start of 21th century energy has become inevitable for mankind, secure and accessible supply of energy is crucial for the sustainability of modern societies (Abbasi 2009). Energy has become an important prerequisite for the socio-economic development of a country, improving quality of life and is extremely crucial for continuum human development in all countries (Afghan et al. 2000).Energy provides a myriad of benefits, it helps to stimulate economic growth and provides power, such as electricity and transportation fuel, that support the well-being and living standards of people around the globe. Energy will help people to become more productive in their work and to raise their income (European Commission 2007).

Throughout the course of history, with the evolution of civilizations, the human demand for energy has continuously risen (Decleris 2010). The global demand for energy is rapidly increasing with increasing human population, urbanization and modernization. The growth in global energy demand is projected to rise sharply over the coming years (Nikolopoulos 2008).

Humans are also constantly interacting with the environment in order to fulfill his needs and in the result altering the environment causing environmental pollution (Manisha 2009). Earth is recently facing the danger of 3 P's, poverty, pollution, population. Among this environmental pollution is one of the biggest problems the world faces today. It is an issue that troubles us economically, physically and everyday of our lives. Pollution mostly occurs due to the overuse of resources and the expanding anthropogenic activities. Although pollution had been known to exist for a very long, it had seen the growth of truly global proportions only since the onset of the industrial revolution during the 19th century. The industrial revolution brought with it technological progress such as use of renewable and non-renewable resources of environment, for example the use of energy has been virtually universal throughout the globe (Modinos 2008).

The world heavily relies on fossil fuels to meet its energy needs, fossil fuels such as oil; gas and coal are providing almost 80% of the global energy demands. On the other hand presently renewable energy and nuclear power are, only contributing 13.5% and 6.5% of the total energy needs respectively (Tingem & Rivington 2005).Energy use and supply is of fundamental importance to society and, with the possible exception of agriculture and forestry, has made the greatest impact on the environment of any human activity, as a result of the large scale and pervasive nature of energy related activities (UNDP 2007).

Impact of Conventional Energy Sources on Environment

The enormous amount of energy being consumed across the world is having adverse implications on the ecosystem of the planet. Fossil fuels, the main source of energy, are inflicting enormous impacts on the environment. Climatic changes driven by human activities, in particular the production of Greenhouse Gas emissions (GHG), directly impact the environment. According to World Health Organization (WHO) as many as 160,000 people die each year from the side-effects of climate change and the numbers could almost double by 2020. These side effects range from malaria to malnutrition and diarrhea that follow in the wake of floods, droughts and warmer temperatures (WHO 2010).

Although energy and environment concerns were originally local in character, for example, problems associated with extraction, transport or noxious emissions - they have now widened to cover regional and global issues such as acid rain and the greenhouse effect. (Hainies *et al.* 2006). Such problems have now become major political issues and the subject of international debate and regulation. It is for this reason that there is a need for an alternative energy that would be environmental friendly (Dincer 2008).

Energy Crisis

On the other hand presently employed energy systems will be unable to cope with future energy requirements fossil fuel reserves are depleting, and predominantly the developed countries employ nuclear power. Fossil fuel and nuclear energy production and consumption are closely linked to environmental degradation that threatens human health and quality of life, and affects ecological balance and biological diversity. It is therefore clear that if the rapidly increasing global energy needs are to be met without irreparable environmental damage, there will have to be a worldwide drive to exploit energy systems that should not endanger the life of current and future generations and should not exceed the carrying capacity of ecosystems (Koukios 2009).

Energy efficiency plays an important role in reducing fossil energy consumption, thus reducing air pollution and slowing down anthropogenic climate change. Accordingly, several countries have formulated political, economic and technical strategies across all sectors of the economy with an aim toward reducing energy demand (Sims 2010).

World primary energy demand is projected to expand by almost 60% from 2002 to 2030, an average annual increase of 1.7% per year. Demand will reach 16.5 billion tons of oil equivalents compared to 10.3 billion to in 2012. The projected rate of growth is, nevertheless, slower than over the past three decades, when demand grew by 2% per year. On the other hand, fossil fuels will continue to dominate global energy use. They will account for around 85% of the increase in world primary demand over 2002–2030. And their share in total demand will increase slightly, from 80% in 2008 to 82% in 2030. The share of renewable energy sources will remain flat, at around 14%, while that of nuclear power will drop from 7% to 5% (Tucker 2007).

Oil will remain the single largest fuel in the global primary energy mix, even though its share will fall marginally, from 36% in 2008 to 35% in 2030. Demand for oil is projected to grow by 1.6% per year, from 77 mb/d in 2002 to 90 mb/d in 2010 and 121 mb/d in 2030. Oil use will become increasingly concentrated in the transport sector, which will account for two-third of the increase in total oil use. Transport will use 54% of the world's oil in 2030 compared to 47% now and 33% in 1971. In OECD countries, the use of oil in the residential and services sector will decline sharply. In non-OECD countries, transport will also be the main driver of oil demand, though the industrial, residential and services sectors will also see steady oil-demand growth. In many developing countries, oil products will remain the leading source of modern commercial energy for cooking and heating, especially in rural areas (Wentzel & Pouris 2007).

So, it is the clarion call at this moment of time in particular, as approaching to the threshold limit of Energy Lead Time in terms of fossil fuels production and consumption as the primary energy source, to intensify our efforts in exploring, building and developing technologies for harnessing natural resources in sustainable energy production. The global energy situation is reaching a crisis point both in terms of sustainability and climate change due to emissions of greenhouse gases; and furthermore depletion of fossil fuel would only be faster considering the kind of development and pace of energy consumption worldwide. A number of recent studies stressed the importance of using innovative technologies to meet the energy needs of the world population. Newer technologies are needed in the area of using coal and thorium on conventional fuels for power generation in mid century term during the Energy Lead Time, while raising contribution of renewable, non-conventional and sustainable energy resources from 8% now to 12% - 15% in next two decades in evolving energy portfolios of 21st century. Coal is still the largest fossil fuel available worldwide, but needed technology to make it a clean energy source (IEA 2005).

Alternative and Environment Friendly Sources of Energy

In future the world's energy supply must become more sustainable (Nandwani 2008). This means that it must meet the basic needs of the poor worldwide without using up in this process the limited natural resources to the detriment of future generations. This can be achieved either by a more efficient use of energy and by relying on renewable sources of energy, particularly wind, hydropower, solar and geothermal energy or by using alternative fuel like biofuels (Kalogirou 2009).

Biofuels as Green fuel

Several factors, particularly increase in energy prices have increased market volatility, in particular during 2008 and 2009; heavy dependence of many countries on imported oil; lingering debate about the ultimate size of remaining, recoverable fossil fuel reserves; and, not least, growing concerns about the environmental impact of fossil fuel usage have provided the impetus for the current strong interest in, and support for, biofuels in many parts of the world. The contribution of biofuels as an alternative energy source is currently very small, but this may change, should the high growth rates of the last few years be sustained in the coming years and decades (Koukios 2009).

Because biofuels are seen as a clean alternative to fossil fuels, there are numerous environmental benefits associated with the use of biofuels; even in the blended form it has advantages over petroleum diesel fuels. It is both non-toxic and biodegradable. It is nearly free of sulphur and carcinogenic benzene, two of the components of petroleum diesel that federal and state initials have regulated because of environment and health concerns. In this regard several countries have initiated policies to provide generous government support to biofuel development and production. A number of countries have also established a regulatory framework to promote and facilitate the use of biofuels in the domestic transportation sector. However, there are growing concerns about the overall energy efficiency of different feedstock, the life cycle environmental benefits of biofuel production and use, the economic rationale of these alternative sources of energy, and the implications for food security and prices (Angina *et al* 2009).

The world is on the verge of an unprecedented increase in the production and use of biofuels. Rising oil prices, national security concerns, the desire to increase farm incomes and a host of new and improved technologies are propelling many governments to enact powerful incentives for using these fuels, which is, in turn, sparking a new wave of investment. Biofuels have the potential to help meet many challenges that the global community faces today, reducing the threat of climate change, reducing reliance on oil and improving international security and alleviating poverty in some of the poorest nations. Among the main economic and security advantages of biofuels are their potential to reduce costly oil imports, decrease vulnerability to price shocks and disruptions in energy supply and increase domestic access to energy. These advantages can benefit both industrialized and developing countries. In general, industrialized countries have the option of either producing biofuels domestically or importing them on a large scale as a substitute for green house gas intensive and increasingly expensive petroleum fuels. In developing countries, as biofuel industry is locally oriented, in which farmer owners produce fuel on their own use is more likely to guarantee benefits to a rural community, promising to be a more directed way of alleviating poverty, especially in more remote oil-dependent regions (Barnwal & Sharma 2004).

Biofuels can be classified into ethanol and biodiesel.

Ethanol and biodiesel ar liquid biofuesl most widely used for transport today, as, ethanol is currently producing from sugar or starch crops while biodiesel is produced from different oils (Dunn & Knoth 2001).

Biodiesel

Biodiesel is a renewable diesel substitute and it also enhances the combustion characteristics of diesel. Biodiesel has three large advantages over regular petroleum diesel. First, it is not a petroleum –based fuel, which means by using biodiesel would reduce our dependency on foreign oil. Second, biodiesel is produced domestically, which means that using biodiesel wills create jobs and contribute to local economies (Fedaro et al 2006). The third major advantage is that it is a cleaner fuel, producing significantly less harmful emissions. Reduction in unburnt hydrocarbons, almost no sulphur oxide emissions and lower carbon mono oxide emissions are associated with the use of biodiesel. When compared to petro-diesel, it reduces emission of particulate matter by 40 %, sulphates by 100 % and carcinogenic PAHs by 90% on an average (Lebedevas 2006). Tests have shown that biodiesel has similar or better fuel consumption, horsepower and torque rates as conventional fuels. The concept of biodiesel as an alternative fuels is not contemporary in its nature, it has been existed for many years but the problem for its promotion is the selection of feedstock (Demirbus 2003). The main commodity sources for biodiesel is non-edible oils obtained from plant species such as Jatropha Curcas (Ratanjyot), Pongamia Pinnata (Karanj), Calophyllum inophyllum (Nagchampa), Hevca brasiliensis (Rubber) etc. According to ASTM standards Biodiesel is technically defined as ,"the mono alkyl esters of long chain fatty acids derived from renewable liquid feedstock, such as vegetable fats and animal oils ,for use in compression ignition (CI) engines". United State produces biodiesel from edible oil (mainly soya oil), the pure biodiesel costs around $ 1.4. Non-edible oils such as Mellia azadirachta (Neem), Bussia Latifolia (Mahua),Pongamai Pinnata (Karanja), Orbignaya maritiana (Babassu), Ratanjyot (Jatropha), etc. are easily extracted in many parts of the world including Pakistan, and are relatively cheap compared to edible oil (Schuchardt *et al.* 2008). While Pakistan is short of petroleum reserve, it has large arable land as well as good climatic conditions (tropical) with adequate rainfall in large regions to account for relatively large biomass production each year. Since edible oil demand being higher than its domestic production, there is no possibility of diverting this for production of biodiesel. Fortunately there is a large region of degraded forest land unutilized public land, field boundaries and fallow lands of farmers where non- edible oil-seeds can be grown. The use of waste material as a source of alternative fuel is a practice of increasing popularity among the researchers worldwide. One such high value waste product is waste cooking oil (WCO) or abused fryer oil. According to INE (Spanish National Institute of statistics) about 74,000,000 lt. of waste olive oil collected every year and discarded inappropriately.

With the mushrooming of fast food centers and restaurants in Pakistan, it is expected that considerable amounts of used-frying oils will be discarded into the drains. These can be used for making biodiesel, thus helping to reduce the cost of water treatment in the sewerage system and assisting in the recycling of resources. Generally cooking oil used for frying are sunflower oil, palm oil, coconut oil etc. as they are easily available, and especially so of the coconut oil which is abundantly available in south India. It is well known fact that, when oils such as these are heated for an extended time (abuse), they undergo oxidation (degradation) and give rise to oxides. Many of these such as hydroperoxides, epoxides and polymeric substances have shown adverse health/biological effects such as growth retardation, increase in liver and kidney size as well as cellular damage to different organs when fed to laboratory animals. An alternative to prevent inappropriate disposal of WCO is by recycling it. The main use of recycled WCO is in the production of animal feeds and in much smaller proportion in the manufacture of soaps and biodegradable lubricants. Some health risks can be traced from the use of recycled cooking oils in animal feeding, such as undesirable levels of contaminants, particularly PAHs (Polycyclic aromatic hydro- carbons), PCBs (Polychlorinated biphenyls), dioxins and dioxin related substances. By consumptions of animal origin foodstuffs like milk, meats, poultry and other products, these undesirable contaminants enter the human body and causing serious illness and health hazards. As these contaminants are liposoluble, they accumulate in organic lipids and finally in the body, and thereby their concentration increases gradually over the years. In other words, the body is exposed not only to a single acute action, but also to a chronic action of bioaccumulation of these hazardous compounds over the years. Hence utilizing the recycled WCO in any way is not advisable from health standpoint. Besides the ill health effects of these WCO (abused oils), their disposable could also have a large environmental implication, because of high COD (Chemical oxygen demand to $2.4 per gallon depending upon purchase volume and the delivery costs and competes with low sulfur diesel oil. However, it is costlier to normal diesel which is $1.2 to $1.5 per gallon. In Pakistan the production of biodiesel from edible oils is currently much more expensive than petroleum diesel fuels due to the relatively high costs of vegetable oils. The cost of biodiesel can be reduced if non-edible oils, andused frying oils are considered instead of edible oils (Knoth *et al.* 2007.

Current Scenario of Biofuels in Pakistan

Pakistan, being an agro-based economy, has great potential in biofuels. Along with ethanol, biodiesel is the most promising renewable fuels derived from various waste oils and vegetable sources that can be used as a substitute or component of diesel (Venkataraman 2002). Biodiesel is a relatively new fuel in Pakistan and not yet commercially available, although it is being already promoted in some pilot projects but due to the economic crisis these projects could not be yet accomplished. Exploiting the large resource potential for biofuels production in Pakistan is also hampered mainly by lacy of information, the absence of set policies and regulations makes investment in the biofuel sector difficult, as the prospective return on investment remains largely unclear. The need of time is that these opportunities must be clearly identified on a case to case basis until the Pakistan government has committed itself to actively promoting development of the national biofuel sector and biofuel market (Abbasi 2009).

Production Processes of Biodiesel

Biodiesel is made by chemically combining the oil with an alcohol in a process known as transesterification. The resulting biodiesel is an alkyl ester of fatty acid, which contain an alcohol group attached to a single hydrocarbon chain comparable in length that of diesel ($C_{10}H_{22}$ to $C_{15}H_{32}$) . The reaction can happen by heating a mixture of 80 to 90 % oil, 10 to 20 % methanol and catalysts. Methanol has been commonly used alcohol in commercial. Production of biodiesel, in part because it has typically been less expensive than ethanol. But there are also technical concerns in using ethanol such as greater difficulties in separating the glycerin by-product from the biodiesel, as well as a propensity for higher process energy costs.

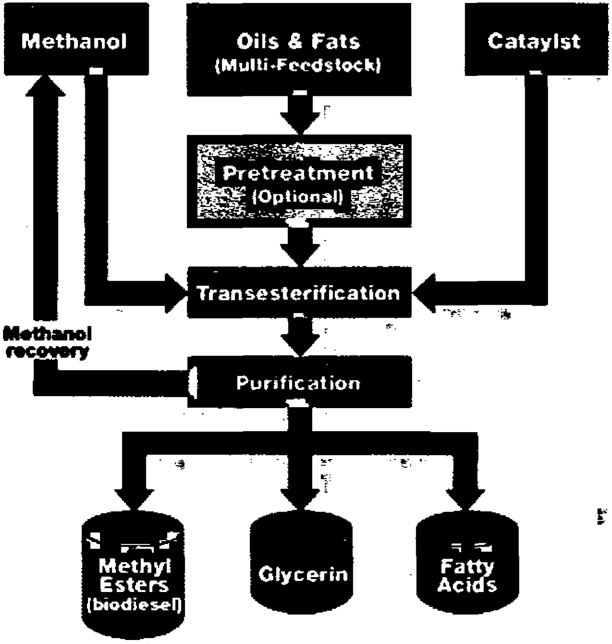


Figure 1.1: Graphical representation of biodiesel production

Catalyst selection for production of biodiesel has been one of the major and controversial debates since the start of biodiesel. Earlier conventional method gained attention comprises of two separate reactions.

➢ Fatty Acids	Biodiesel	Sulphuric Acid
➢ Triacylglycerols	Biodiesel	NaOH,KOH

Sodium hydroxide/potassium hydroxide and sulfuric acid are not compatible with each other, so the reactions must be carried out in separate vessels. That makes the process less efficient.

To find a better way, Sello and Socha were the first to use the method of catalytically conversion and went looking for catalysts that would be cheap, chemically stable and of limited toxicity. In addition, they performed the reactions using a microwave reactor instead of a conventional thermal heater. They used bismuth triflate and scandium triflate, commonly used as catalysts. Catalysts converted waste vegetable oil into biodiesel without any combustion and the chemists also were able to perform the conversion in one reaction vessel, since the catalysts can promote both the reaction that converts free fatty acids into biodiesel and the reaction in which triacylgycerols are converted to biodiesel. But the major problem was the long reaction time (Sello % Socha 2000).

The use of alkali catalysts in the tansesterification of used cooking oil is somewhat limited because the FFA in used cooking oil reacts with the most common alkaline catalysts (NaOH, KOH, and CH3ONa) and forms soap. Because water makes the reaction partially change to saponification, the alkali catalyst is consumed in producing soap and reduces catalyst efficiency. The soap causes an increase in viscosity, formation of gels which reduces ester yield and makes the separation of glycerol difficult. These two problems notwithstanding, literature is repeled with studies on the transesterification of waste cooking oil using alkaly catalyst (Arquiza et.al 2003).

Despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman investigated the transesterification of soybean oil with methanol using 1 wt. % concentrated sulfuric acid (based on oil). They found that at 65 C and a molar ratio of 30:1 methanol to oil, it took 69 h to obtain more than 90% oil conversion to methyl esters (Freedman *et al.* 2002).

As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems. To date it has only been carried out on the laboratory scale and therefore will not be further discussed herein (Watanabe *et al.* 2001).

Fisher-tropsh catalyst has been used extensively .These catalysts produces a petroleum substitute, typically from coal, natural gas or biomass for use as synthetic lubricant oil and as synthetic fuels and received intermittent attention as a source of low-sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons. Many scientists studied the influence of these catalyst and temperature on yield and product composition during gasification. They used temperature range of 750 - 950°C. However, reactions catalyzed by theses catalysts were very slow owing to the low surface area of the catalyst (Pinto 2005).

All methods for the production of fuels have their own limitations but for better fuel formation, so there is strong need to develop new green catalyst that should be efficient, involve an easy work-up and afford greater yields in shorter reaction times.

Nanotechnology:

Nanotechnology is making the leap from science fiction to science reality. The overwhelming majority of people have not yet noticed this transition but the technology of the vanishingly small will be expansively influential in the next couple of decades. For it is not just a new range of technologies but a new social force: a driver of techno-social-culture change (Schelenk 2005). Nanotechnology emerged as overseen solution to all the above problems and changed the technology how the biodiesel was produced previously, making biodiesel production dramatically better, cheaper and faster (Du *et al.* 2004). Nano catalysts have high specific surface and high catalysis activities, may solve the above problems. They have become the focus of recent research. Nano particles, in particular being cheap, need mild reaction conditions for high yields of products in short reaction times as compared to the traditional catalysts. For example, Co or Co oxide nanostructures are known to be effective catalysts. This technology replaces the commonly used sodium meth oxide, a toxic, corrosive and flammable catalysts in biodiesel production and eliminates several production steps including acid neutralization, water washes and separation (Noureddini *et al.* 2005).

A large number of methods is emerging as synthetic routes for the preparation of nano catalysts. These include: mechano chemical synthesis, sol-gel process, hydrothermal process, Chemical vapor condensation, laser pyrolysis, precipitation. Comparatively, each method has advantages and disadvantages. In this particular research activity precipitation method followed by hydrothermal process has been utilized to produce cobalt, nickel, copper cerium and copper-nickel nano particles (Fosberg et al. 2006).

1.1 Significance of Study

Energy is inevitable for mankind, secure and accessible supply of energy is crucial for the sustainability of modern societies. The world heavily relies on fossil fuels to meet its energy needs. Fossil fuels such as oil, gas and coal are providing almost 80% of the global energy demands. Energy crisis, Global warming, have pushed the countries to seriously consider finding and creating new and reliable sources of energy that not only are renewable but also are friendly to the environment. Biofuels emerged as a cheap and most popular source of alternate fuels gaining increased public and scientific attention, driven by factors such as:

Biodiesel is a renewable, biodegradable, environmentally benign, energy efficient, substitution fuel which can fulfill energy security needs without sacrificing engine's operational performance. Thus it provides a feasible solution to the twin crises of fossil fuel depletion and environmental degradation (Hama *et al.* 2004). Various modern techniques are employed now a day to produce biodiesel. Most commonly transesterification method used involves stripping the glycerin from the fatty acids with a catalyst such as sodium hydroxide and replacing it with an anhydrous methanol. The resulting raw product is then centrifuged and washed with water to cleanse it of impurities. This yields methyl ester (biodiesel), as well as a smaller amount of glycerol and soap. It is very difficult to separate these by-products from the biodiesel requires hours of washing and filtration. To overcome this problem and presenting the best biodiesel in foreseen future this particular work was designed for the production of biodiesel with new and advance technology of nano catalysts without any by-products and for the comparison basis various conventional methods were also been adopted. Pure metallic nano catalysts were prepared and characterized for their morphology, structure, physical parameters, surface details, shape and size of the particles as well as the crystal properties and furthermore their role in conversion of waste cooking oil into biodiesel.

1.2 Aim and Objectives of the Study

To develop an environmentally benign and technically simple way to convert waste cooking oil into biodiesel so that the production of energy at the expense of the environment is untenable and should be avoided at all costs.

Objectives of the present study are:

- To synthesize cobalt oxide, nickel oxide , copper cerium oxide and copper nickel oxide nano particles.
- Development of process to utilize the synthesized catalysts for production of biodiesel from waste cooking oil.
- Comparison of nanocatalytical conversion of waste cooking oil into biodiesel with conventional alkali conversion method

CHAPTER #2

EXPERIMENTAL

2 EXPERIMENTAL

2.1 Materials and Reagents

All the glassware with standard quick fit joints was used throughout the work after, washing with detergents, rinsing with acetone and drying in an oven at 120 °C. The glassware which was utilized during the research work includes beakers, funnels, three necked flasks, volumetric cylinders, condensers and glass rods. These were of Witeg; Germany Ltd. Reagents used were of analytical grade. Cobalt nitrate hexa hydrate (Fluka 98.0%), Nickel nitrate hexa hydrate (Riedel 99.99%), Cerium sulphate pentahydrate (Merck 98.5%) Copper nitrate (Aldrich 98%) Sodium hydroxide (NaOH) (Fluka 97%), Sulfuric acid (H_2SO_4), Nitric acid (HNO_3) (Fluka 96%) Copper (II) nitrate dihydrate ($CuCl_2.2H_2O$) (Aldrich 99%) were used. All the solvents were used of 99% pure. Methanol was obtained from E. Merck (Germany). Ethanol was obtained from PS (Panrireac Sintesis). Absolute acetone was obtained from Riedel de Haen.

2.2 Instrumentation

- **XRD:** Philips X'pert PRO 3040/60 difractrometer with radiation source operated at 40kV and 30 mA.
- **FTIR:** BIO- RAD EXCALIBUR FTS 3000/016-0221-2.
- **GC/MS:** GC-6890 N directly uploaded to MS 5973 MSD 01ul.The MS was set to range of m/z 02-600 and ionization potential.
- **NMR:** NMR spectra ('H & C) were recorded by Bruker ARX-300 MHz.

2.3 Sample Collection

The samples of waste cooking oil were collected from KFC outlet at F-6/2 and F-10 markaz Islamabad.

2.4 Pre-Treatment Process

2.4.1 Removal of Solid Contents

Solid contents were removed by simple process of filtration. The filtration was carried out by whatman filter paper depending on the oil quality and density.

2.4.2 Removing Moisture Contents of Crude Oil

Filtered oil was heated up to 100 °C in order to reduce the moisture content of crude oil. Since water causes the triglycerides to hydrolyze forming soap contents instead of undergoing transesterification to give biodiesel, therefore it is necessary to remove the water contents.

2.4.3 Determination of Acid Value of Oil

The acid value of oil was determined by simple acid base titration. Two types of titrations were performed, blank titration and sample titration. In blank titration only THF and methyl orange were taken in flask and titrated against potassium hydroxide till the color of methyl orange was changed from orange to yellow indicating the end point. In sample titration THF, sample of oil and methyl orange as an indicator were taken and titrated against potassium hydroxide till the color was changed indicating end point. Acid value was calculated using formula:

$$(A-B)\ N \times 56.1/W$$

Where, A= milliliters of potassium hydroxide used for sample.

B= milliliters of potassium hydroxide used for blank.

N= normality.

W= grams of oil.

2.4.4 Determination of Fatty Acid Contents

Percentage of fatty acid was estimated by multiplying the acid value with factor 0.503

Percentage of free fatty acids (FFA) = 0.503 × Acid value.

2.5 Nano Catalyzed Biodiesel

2.5.1 Preparation of Cobalt Oxide Nano Catalysts

The Co nano particles were prepared by precipitation from aqueous solution, in which the reactants were mixed in one molar stoichiometric quantity. The starting raw materials was cobalt nitrate hexa hydrate [Co(NO3)2.6 H2O], which was of analytical grade (Sigma). The aqueous solution was mixed in the following order: first, A stoichiometric amount of Cu (NO3)2·6H2O was dissolved in 5 % v/v ratio of conc. nitric acid and distilled water. Secondly, an aqueous one molar solution of sodium hydroxide was added with constant stirring to the above solution mixture until pH > 10 to ensure complete precipitation (Fig. 2.1 for flowchart of preparation). After filtration, precipitate was washed several times and dried in an oven at 100˚C for 12 hrs. The oven dried precursor was calcined at various temperatures ranging from 700 to 900˚C to get phase pure samples.

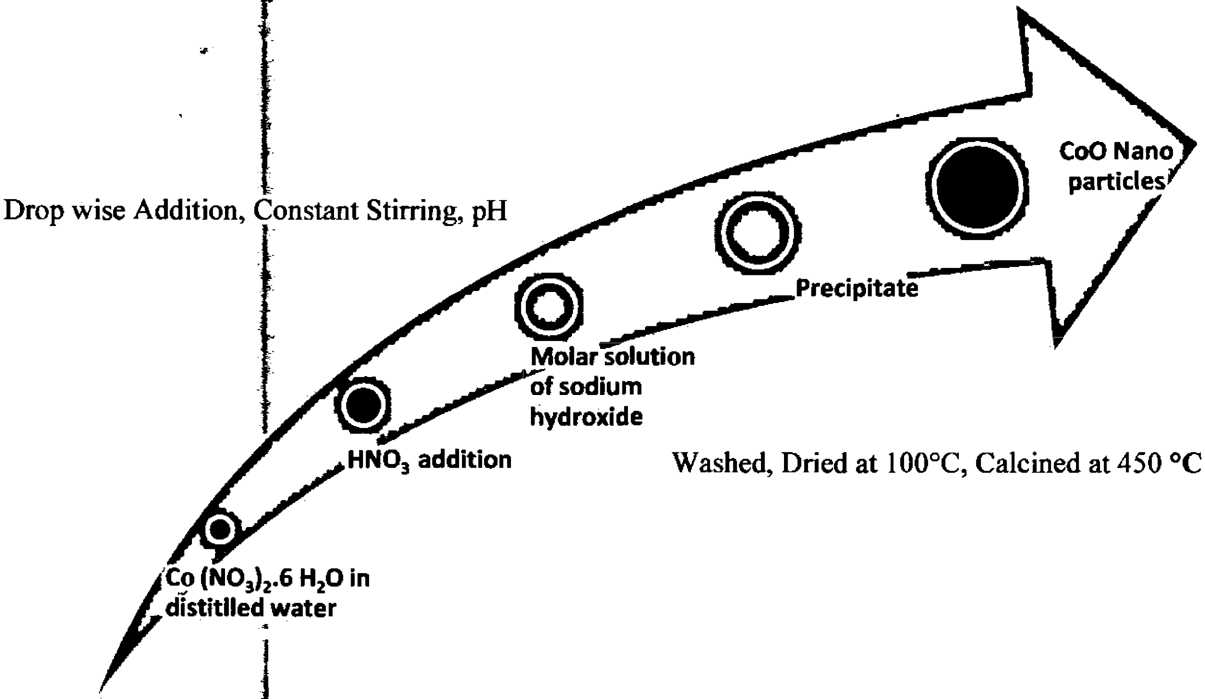


Figure 2.1: Flowchart for the preparation of Cobalt oxide nano particles

2.5.2 Preparation of Nickel Oxide Nano Catalyst

The Ni nano particles were prepared by precipitation from aqueous solution, in which the reactants were mixed in one molar stoichiometric quantity. The starting raw material was nickel nitrate hexa hydrate [$NiNO_3.6H_2O$], which was of analytical grade (Sigma). The aqueous solution was mixed in the following order: first, a stoichiometric amount of $NiNO_3.6H_2O$ was dissolved in 5 % v/v ratio of conc. nitric acid and distilled water. Secondly, an aqueous one molar solution of sodium hydroxide was added with constant stirring to the above solution mixture until pH > 10 to ensure complete precipitation (Fig. 2.2 for flowchart of preparation). After filtration precipitate was washed several times and dried in an oven at 100°C for 12 hrs. The oven dried precursor was calcined at various temperatures ranging from 700 to 900°C to get phase pure samples.

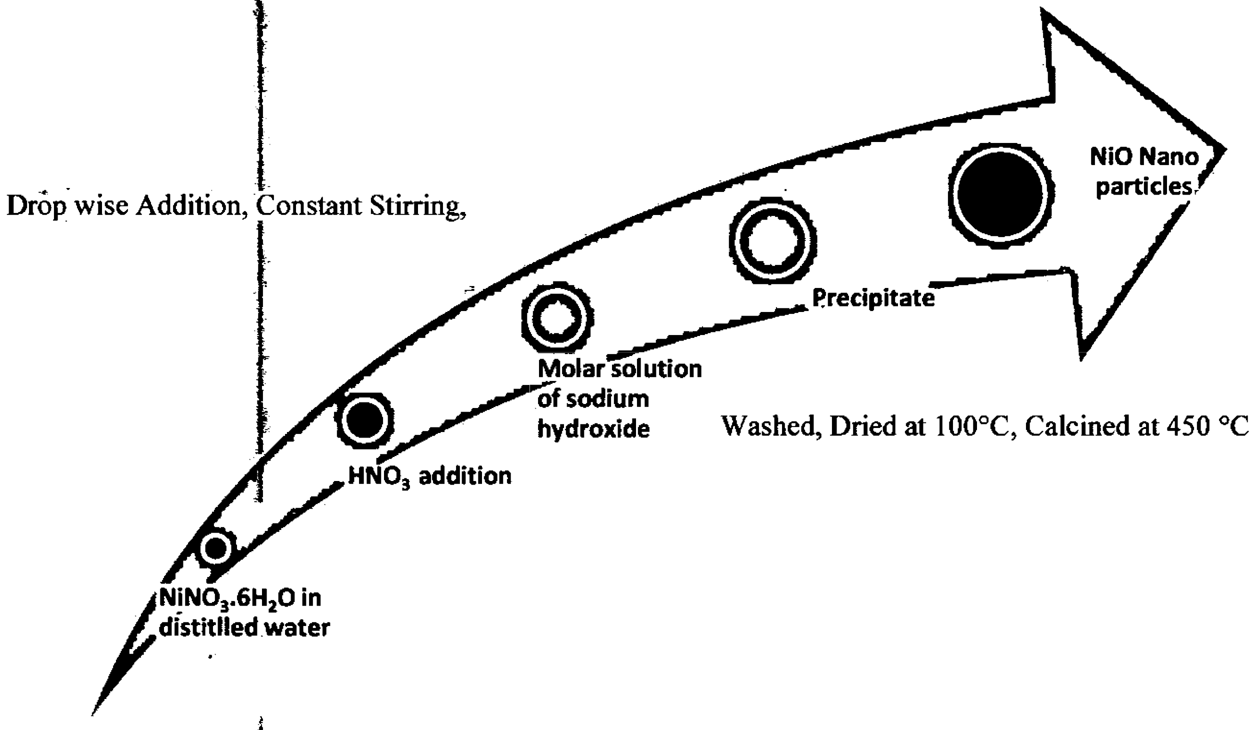


Figure 2.2: Flowchart for the preparation of Nickel oxide nano particles

2.5.3 Preparation of Copper Nickel Nano Composites

The Cu-Ni composites [$Cu_2O.NiO$] were prepared by precipitation from aqueous solution, in which the reactants were mixed in one molar stoichiometric quantity. The starting raw materials were cupper (II) nitrate hexa hydrate [$Cu\ (NO_3)_2.6H_2O$] and nickel (II) nitrate hexa hydrate [$NiNO_3.6H_2O$], which were of analytical grade (Sigma). The aqueous solution was mixed in the following order: first, A stoichiometric amount of $Cu\ (NO_3)_2{\cdot}6H_2O$ was dissolved in distilled water, second, $Ni\ (NO_3)_2{\cdot}6H_2O$ was dissolved in minimum amount of conc. HNO_3 to avoid precipitation of Ni ions. An aqueous one molar solution of sodium hydroxide was added with constant stirring to the above solution mixture until pH > 10 to ensure complete precipitation (Fig. 2.3 for flowchart of preparation). After filtration precipitate was washed several times and dried in an oven at 100°C for 12 hrs. The oven dried precursor was calcined at various temperatures ranging from 700 to 900°C to get phase pure samples.

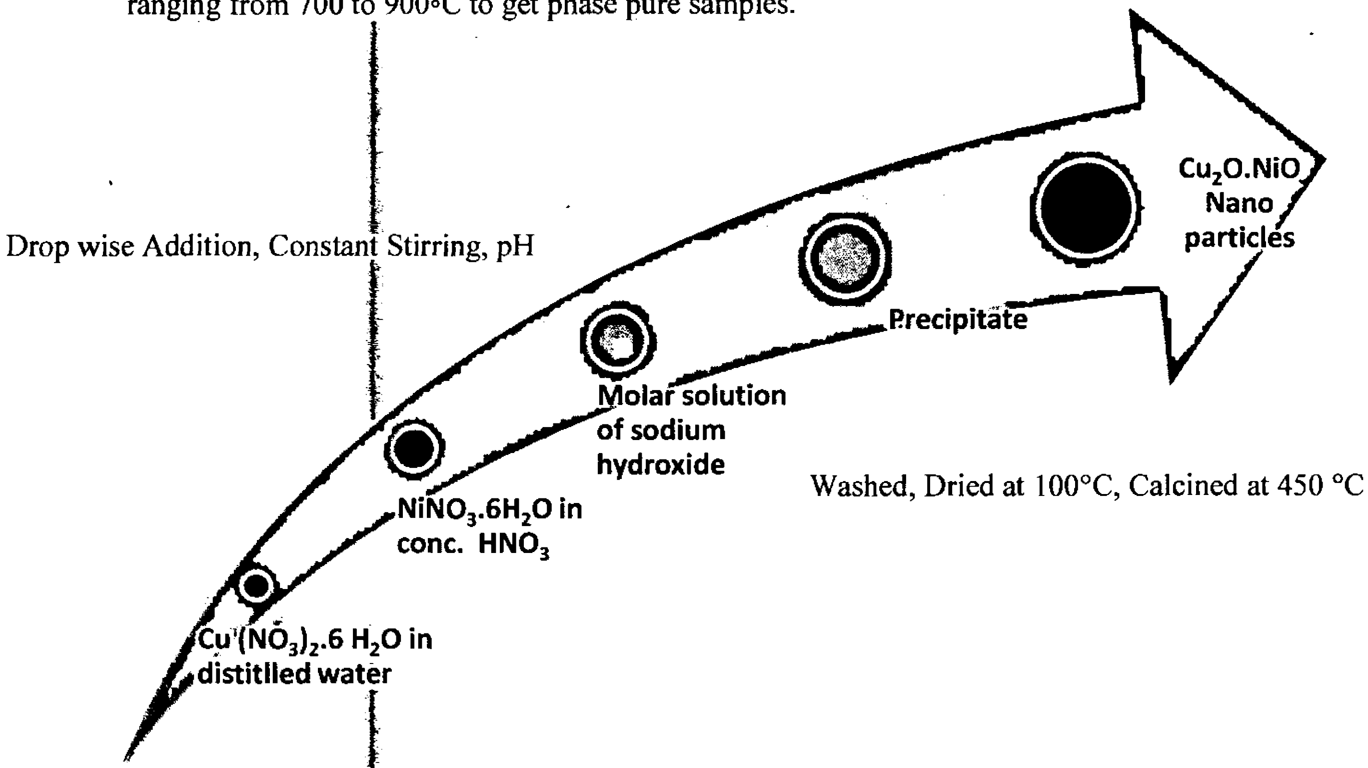


Figure 2.3: Flowchart for the preparation of Copper Oxide-Nickel oxide nano particles

2.5.4 Preparation of Copper Cerium Nano Composites

The Cu-Ce composites [Cu_2O. CeO] were prepared by precipitation from aqueous solution, in which the reactants were mixed in one molar stoichiometric quantities. The starting raw materials were cupper (II) nitrate hexa hydrate [$Cu\ (NO_3)_2.6H_2O$] and cerium sulphate penta hydrate [$Ce(SO_4)_2{\cdot}5H_2O$] ,which were of analytical grade (Sigma). The aqueous solution was mixed in the following order: first, A stoichiometric amount of $Cu\ (NO_3)_2{\cdot}6H_2O$ was dissolved in distilled water, second, $Ce\ (SO_4)_2{\cdot}5H_2O$ was dissolved in minimum amount of conc. HNO_3 to avoid precipitation of Ce ions. An aqueous one molar solution of sodium hydroxide was added with constant stirring to the above solution mixture until pH > 10 to ensure complete precipitation (Fig. 2.4 for flowchart of preparation). After filtration, precipitate was washed several times and dried in an oven at 100°C for 12 hrs. The oven dried precursor was calcined at various temperatures ranging from 700 to 900°C to get phase pure samples. phase pure samples.

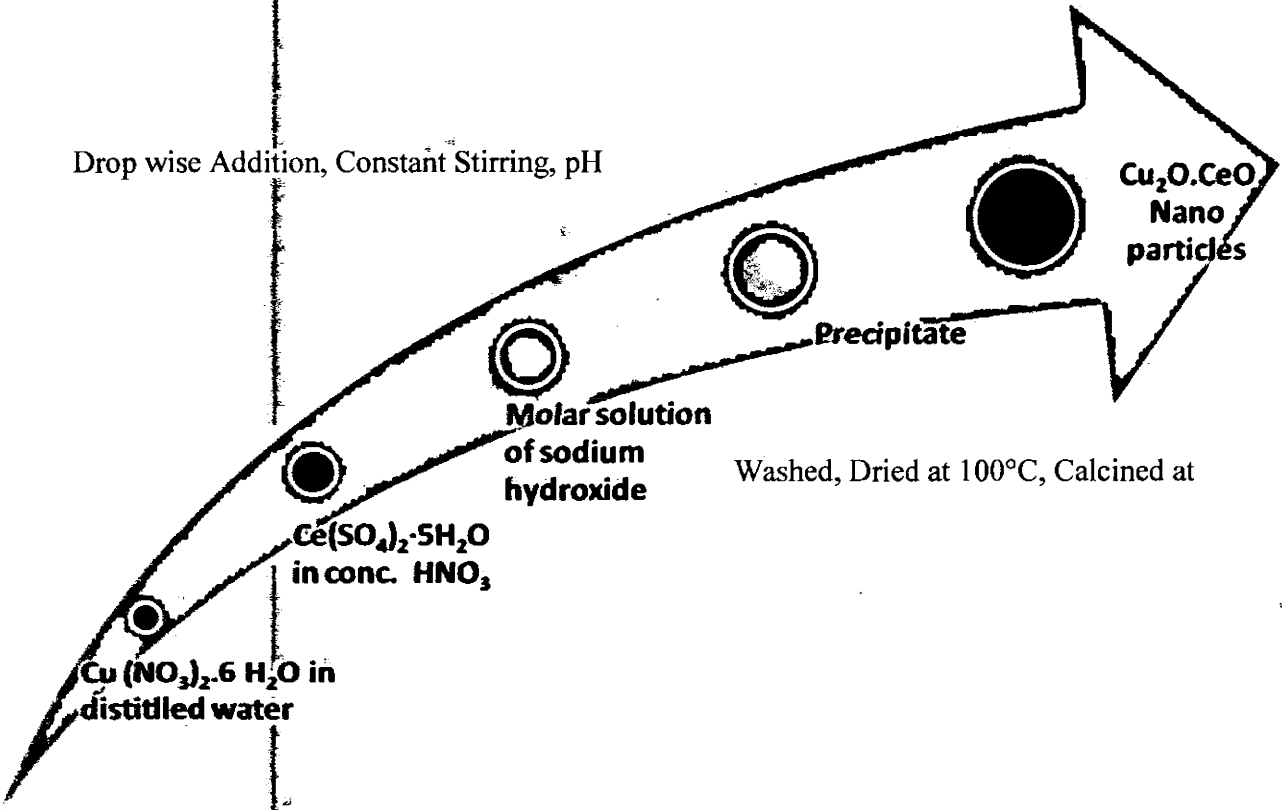


Figure 2.4: Flowchart for the Synthesis of Copper Oxide-Cerium Oxide Nano particles

2.5.5 Production of Biodiesel by Nano Catalysts

In this work nano particles of copper-nickel, copper-cerium, nickel and cobalt were used for the production of biodiesel from waste oil. Accurately weighed quantity of each metallic salt was taken and dissolved in 100 ml of waste oil to prepare 10 % solution this solution was transferred to the parr reactor 30 ml of methanol was added to the above solution the reaction assembly was closed argon gas was passed. Reaction was refluxed for half an hour at 160 ° C. Hydrogen gas was passed at 200 psi, 300 psi and 500 psi. The resulting liquid was filtered, washed for the removal of some by impurities and dried.

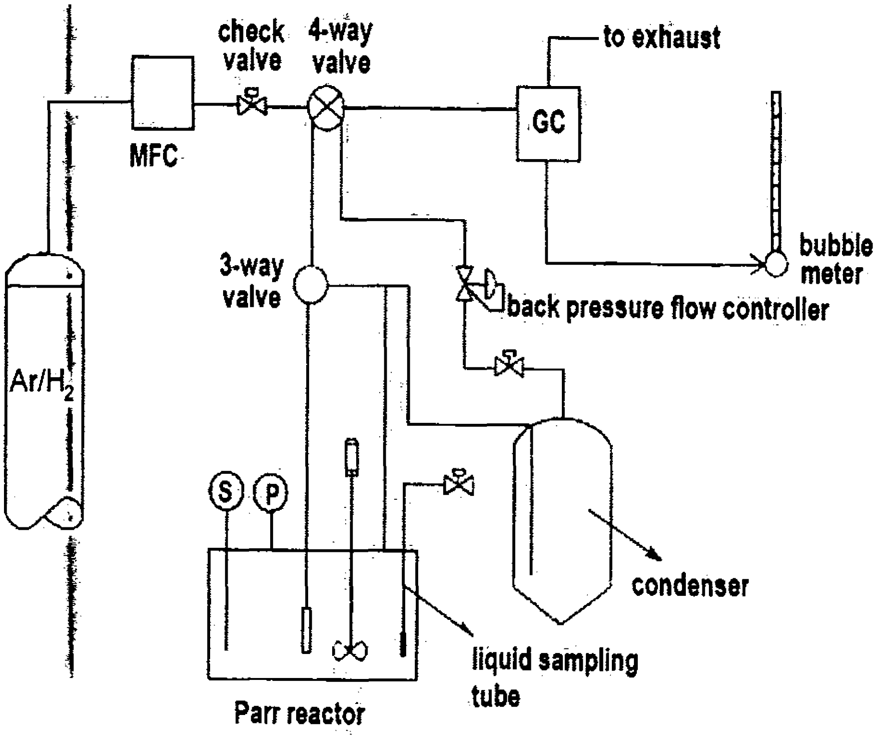


Figure 2.5: Parr Reactor

2.6 Base catalyzed Biodiesel

2.6.1 Study of Effect of Molar Ratio

Three different stock solutions were made by mixing 0.6, 0.8, 1 g of sodium hydroxide in 30 ml of methanol separately to prepare sodium methoxide, a catalyst for transesterification process. The molar ratio of methanol to oil was fixed at 6:1 which is optimal ratio of transesterification. These three catalysts were added to oil separately at 60 ° C with vigorous stirring at which the conversion of triglycerides into fatty acids methyl esters was assumed to be maximum. After that solutions were allowed to settle down for several hours. Glycerin and soap (By products) formed during reaction were separated after settling. Biodiesel floats on the top while the denser glycerin settles at the bottom.

2.6.2 Study of effect of Temperature

Stock solution was made by mixing 1 g of sodium hydroxide in 30 ml of methanol separately to prepare sodium methoxide, a catalyst for transesterification process. The molar ratio of methanol to oil was fixed at 6:1 which is optimal ratio of transesterification. This catalyst was added to three different samples of oil separately at 30 ° C, 40 ° C and 50 ° C respectively with vigorous stirring at which the conversion of triglycerides into fatty acids methyl esters was assumed to be maximum. After that solutions were allowed to settle down for several hours. Glycerin and soap (By products) formed during reaction were separated after settling. Biodiesel floats on the top while the denser glycerin settles at the bottom.

2.6.3 Neutralization and De-sponification of Biodiesel:

Excess methanol, catalysts and soap were removed from fatty acid methyl esters (FAME) by washing with warm water. Water was sprayed on the top of separating column until the ph became neutral. This washed diesel may contain several percent of water. The residual water was eliminated by treating with anhydrous barium sulphate followed by filtration and lowered to a maximum of 0.05 % (v/v) to meet ASTM biodiesel specification.

CHAPTER #3

RESULTS AND DISCUSSIONS

3 RESULTS AND DISCUSSION

Nano transesterification and base treansesterification were carried out and characterized for its quality checking according to ASTM standards. No change in the fuel quality was observed in both transesterification processes, the only change is that our innovative nano technology has reduced the cost of biodiesel by producing no by products giving high yields of biodiesel in lesser time, eliminated water wastage and the most economical fuel by reducing the cost of production Before reaction process, it was ensured that the oil contained very little amounts of water in it because every molecule of water would destroy a molecule of catalyst. The filtered WCO was subjected to drying by heating it to 100 ^{0}C for at least fifteen minutes with continuous stirring. The samples of WCO were decanted and then transesterified using methanol in presence precisely calculated amount of catalyst to get fatty acid methyl ester, which is called as "WCO Biodiesel". The free fatty acid content calculated in the oil used was 64%.

Table 3.1: Fatty Acid Content of the Oil

Sr. No	Fatty Acids	Formula	Percentage
1.	Tetradecanoic acid	$CH_3(CH_2)_{13}COOH$	7.5
2.	9- 11 Hexadedecanoic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_2COOH$	10.7
3.	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	8.78
4.	10, 13-Octadecadienoic acid	$CH_3(CH_2)_3CH{=}CHCH_2CH{=}CH(CH_2)_8COOH$	7.70
5.	Octadecenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	9.73
6.	11-Eicosenoic acid	$CH_2(CH_2)_7CH{=}CH(CH_2)_9COOH$	6.35
7.	Eicosenoic aci	$CH_3(CH_2)_{18}COOH$	4. 3
8.	9-Docosanoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	4. 45
9.	Docosanoic acid	$CH_3(CH_2)_{20}COOH$	5. 27
10.	Tetracosenoic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$	3. 10

3.1 Physical Properties of Biodiesel

Fuel properties such as density, specific gravity, flash point, viscosity and cetane index determined by standard procedure and results are shown in Table 3.1 for comparison. The property values listed in the Table 3.1 were evaluated twice and the values depicted in the below table are that of the average.

Table 3.2: Test Fuel Properties

Fuel Properties	Base Catalyzed Biodiesel	Nano Catalyzed Biodiesel	Standard Biodiesel (ASTM/HSD)
Color	Amber Yellow	Amber Yellow	Amber Yeallow
Kinematic Viscosity	1.87 cs	4.24 cs	1.90 to 6.0 cs
Specific Gravity	0.888	0.901	0.87 to 0.89
Flash Point	132	96	100 to 170
Pour Point	3	5	-15 to 10

ASTM= American Standards Testing Materials

HSD= High Speed Diesel

3.2 Base-Catalyzed Trans-esterification

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. Several transesterification reactions were carried out for studying various aspects including effect of temperature, stirring speed and vegetable oil/ molar ratio of sodium hydroxide. Reaction took 30-40 min depending on the conditions applied. The stoichiometry reaction required 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol was used to increase the an influence on the course of the transesterification. The best conditions for biodiesel were 30ml methanol ratio in 100 ml of oil having 1g of NaOH used at 60 degree centigrade. Influences of stirring speed, temperature and molar ratio to the yield of biodiesel are shown in the figures below.

Stirring speed is also an important factor that influenced biodiesel yield. Each experiment was run for different stirring speed with 1 wt% catalyst and 4/1 molar ratio of methanol/oil. The results shown in figure 3.1 indicates that biodiesel yield is low at low stirring speed with only 52.4% yield at 40 stirs for 30 min. Biodiesel yield increased sharply as stirring speed, and reached 94.2% at 90 stirs. When stirring speed was higher than 95, methanol would vaporize and form a lot of bubbles, which could inhibit reactions on the three-phase interface. Therefore, the optimized temperature was around 95 stirring speed.

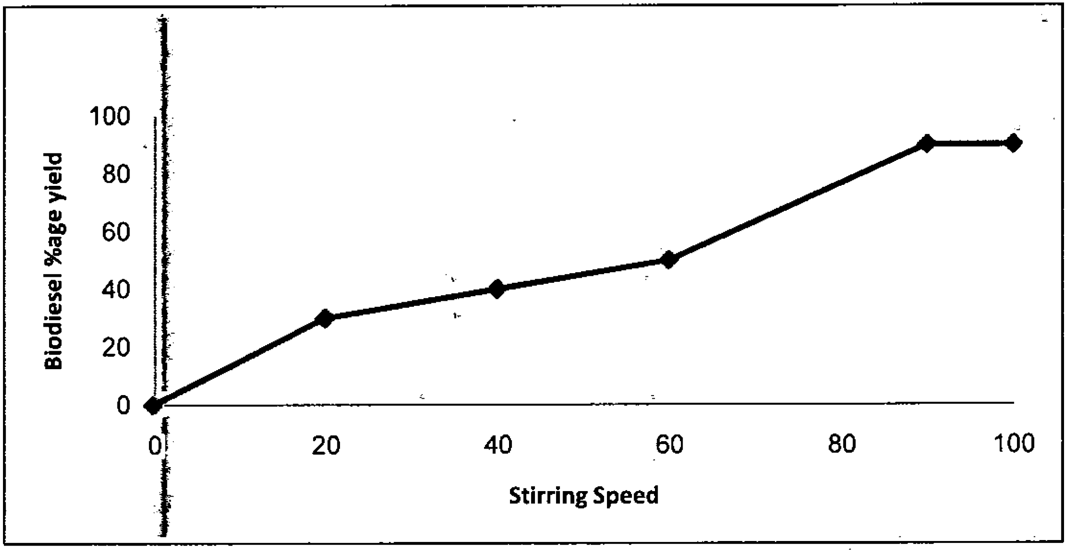


Figure 3.1: Effect of stirring speed on yield of biodiesel

Temperature has detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion (Pinto et al., 2005). Transesterification can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol employed (60 °C in case of methanol) so that the reactor does not need to be pressurized. Thus, the usual temperature used during transesterification in most literature is 60-65 °C. When the reaction temperature closes or exceeds the boiling point of methanol (68 °C), the methanol will vaporize and form a large number of bubbles which may inhibit the reaction (Meng et al., 2008).Various experiments have been carried out to find out the optimum temperature of the transesterification reaction. While transesterification of waste cooking oil was observed and maximum conversion occurred at 60 °C.

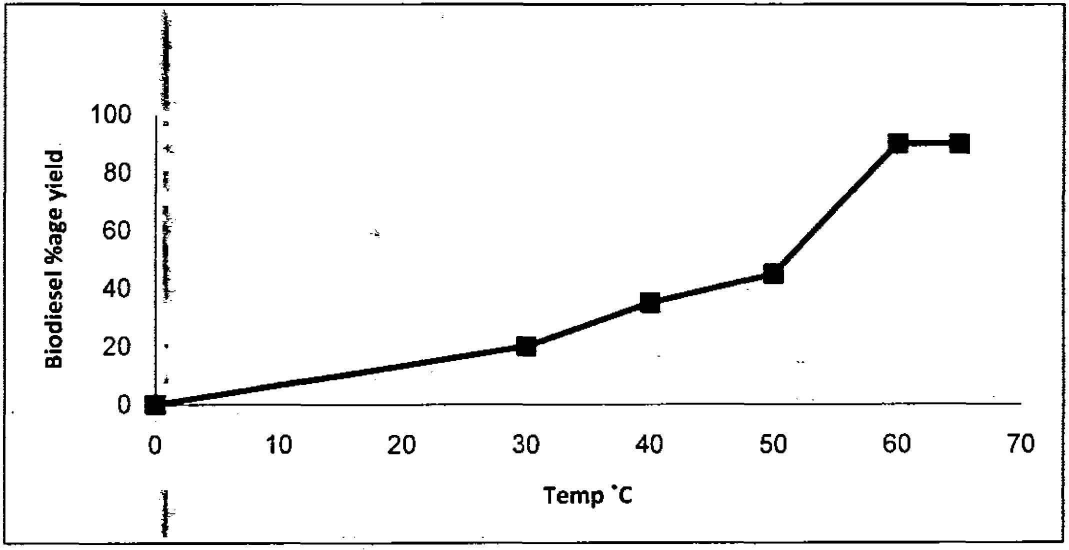


Figure 3.2: Effect of temperature on yield of biodiesel

The molar ratio of methanol/WCO was one of the important factors that affected the yield of methyl esters. Stoichiometrically, 3 mol of methanol were required for each mole of oil (Meng et al., 2008). However, in practice, methanol/oil molar ratio should be higher than that of stoichiometric in order to drive the reaction toward completion and produce more methyl esters. The effects of methanol/WCO molar ratio on biodiesel yield are given in **Fig. 3.3**. When the ratio increased from 0.6g to 0.8g, the yield of methyl esters rose considerably from 50 to60%. Because WCO was immiscible with methanol, the reaction was incomplete and limited by diffusion and thermodynamic process. So, excessive methanol should be used to promote the reaction. The maximum yield of 94.7% was achieved when the molar ratio was close to 1g. Higher molar ratio over the stoichiometric value resulted in a high rate of esters formation and could ensure complete reaction (Pinto et al., 2005). However, it was observed that at molar ratios above 1g, excessive methanol had no significant effect on the yield. Conversely, a longer time was required for the subsequent separation stage because separation of the esters layer from glycerol was difficult due to the fact that methanol with one polar hydroxyl group could emulsify the products **(Sims 2010)**.. Hence, the best methanol/oil molar ratio was selected as 4/1.

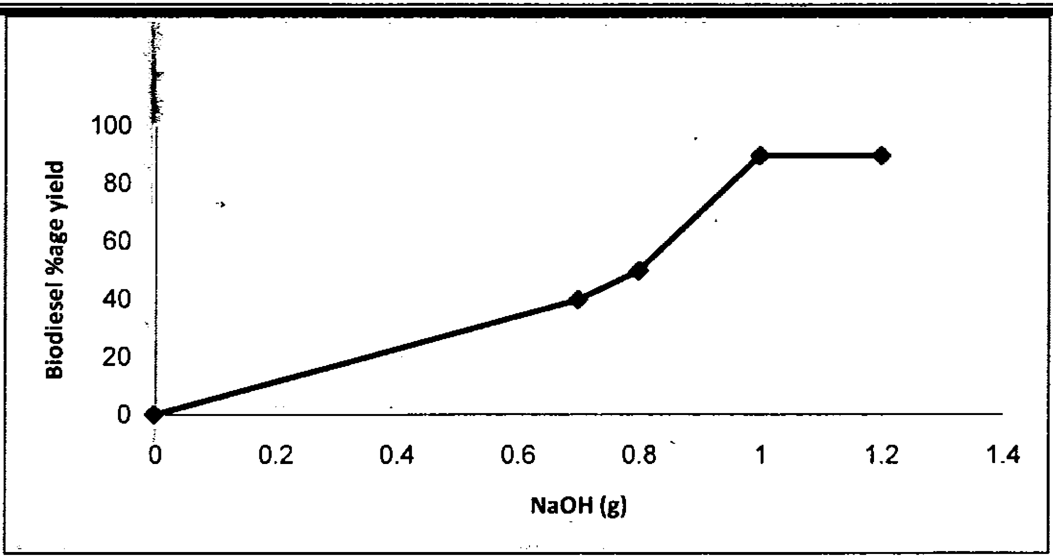


Figure 3.3: Effect of molar ratio of NaOH on yield of biodiesel

3.3 Investigation of Base-Catalyzed Trans-esterifies Biodiesel

The used cooking oil (WCO) has properties different from the properties of refined / crude fresh cooking oils. During frying process; presence of heat and water accelerates the hydrolysis of triglycerides and increases content of free fatty acids in oil. Oxidation stability of the oil is disturbed because of the contact of hot oil with food, and peroxide value of oil increases. Viscosity of oil increases considerably, because of the formation of dimeric and polymeric acids and glycerides Modinos, M. (2008). Correspondingly, molecular mass and iodine value decreases and saponification value and density increases. The free fatty acid and moisture content are important process parameter for the biodiesel production i.e. transesterification process. They are the vital key for determining the viability of the cooking oil transesterification process. Thus the process of biodiesel production from WCO differs from that of fresh oil. The problem with processing WCO is that they usually contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst due to formation of salts (soap) and hence smaller is the conversion efficiency. The soaps prevent separation of biodiesel from glycerin fraction and is in agreement with literatures Gryglewicz, S. (2000). The moisture content in WCO should be removed before starting up the transesterification and excess free fatty acids should be neutralized. In the present study the free fatty acids were naturalized by using additional catalyst (NaOH) and moisture was dried out by heating the feed stock to 100^{0}C for a period of 15 minutes with continuous steering. However, to neutralize the free fatty acids accumulated in the WCO, extreme care has to be taken.

study the free fatty acids were naturalized by using additional catalyst (NaOH) and moisture was dried out by heating the feed stock to 100^0C for a period of 15 minutes with continuous steering. However, to neutralize the free fatty acids accumulated in the WCO, extreme care has to be taken. This is because, during the neutralizing the free fatty acids, as both excess as well as insufficient amount of catalyst may cause soap formation. Hence to determine the correct amount of catalyst required, a titration must be performed on the oil being transesterified were discussed in figures above. One simple method is presented below, using a chemical indicator called phenolphthalein. In the titration, 0.1% of NaOH in distilled water is titrated against the titration sample which is essentially a solution of 10ml of Isopropyl alcohol and 1 ml of oil sample with 2-3 drops of indicator. The end point of the titration is marked when the titration sample turns pink (magenta), and stays pink for 10 seconds. The number of milliters of 0.1% NaOH solution needed is equal to the number of extra grams of pure sodium hydroxide catalyst needed to produce the proper reaction to make biodiesel from WCO. Confirmation of biodiesel was done by using different techniques such as:

- NMR.
- FTIR
- GC/MS

3.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern energy tools, infrared is an excellent tool for quantitative analysis of biodiesel.

Table 3.3: FT-IR studies of Trans-esterifies biodiesel

Sr .No	Functional Group	Observed Frequency	
		Effect of temperature	**Effect of molar ratio**
1.	C=O	1740.69 1745.51	1740.69 1741.68
2.	C-O (asymmetric-symmetric)	1016.57	1014.74
3.	C-O	1195.67	1195.67
4.	CH_2	2923.21 2853.49	2922.88 2853.54
5.	CH (stretching)	3006.70	3006.70
6.	CH_3 (bending)	1360.89 1435.83 1460.21	1360.88 1435.84 1460.09
7.	CH_2 (bending)	1169.31	1168.87
8.	CH (bending)	721	721.77

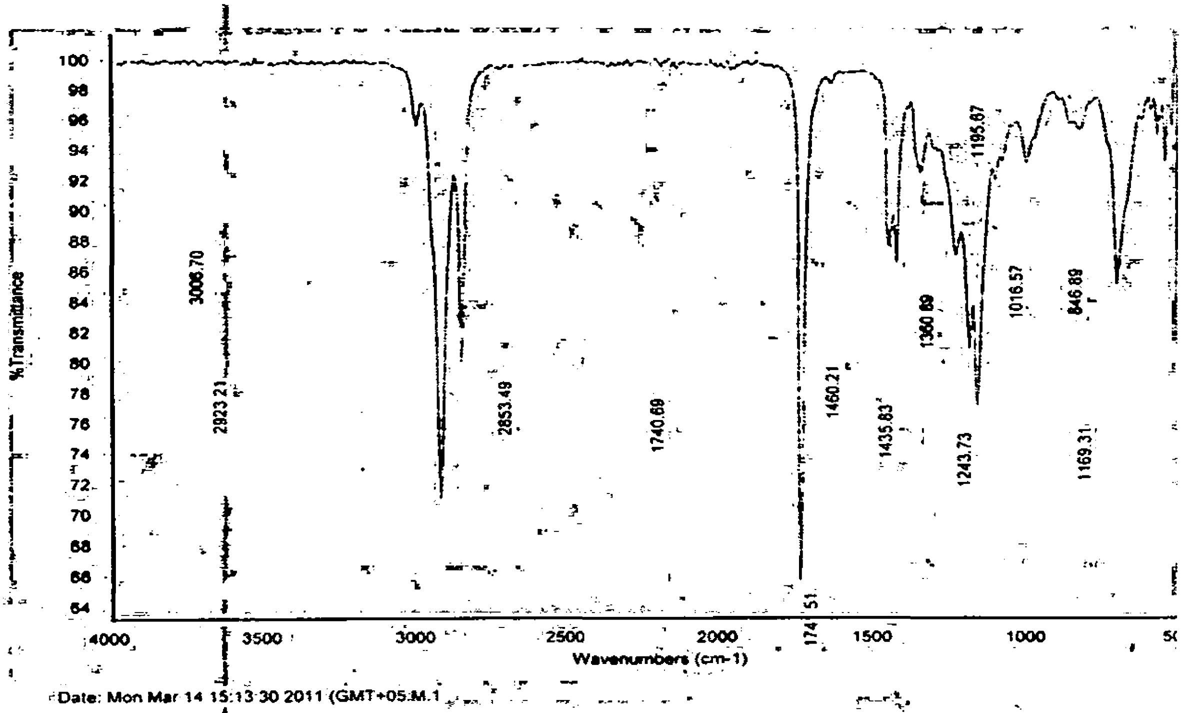


Figure 3.4: FT-IR spectra of Trans-esterifies biodiesel for temperature.

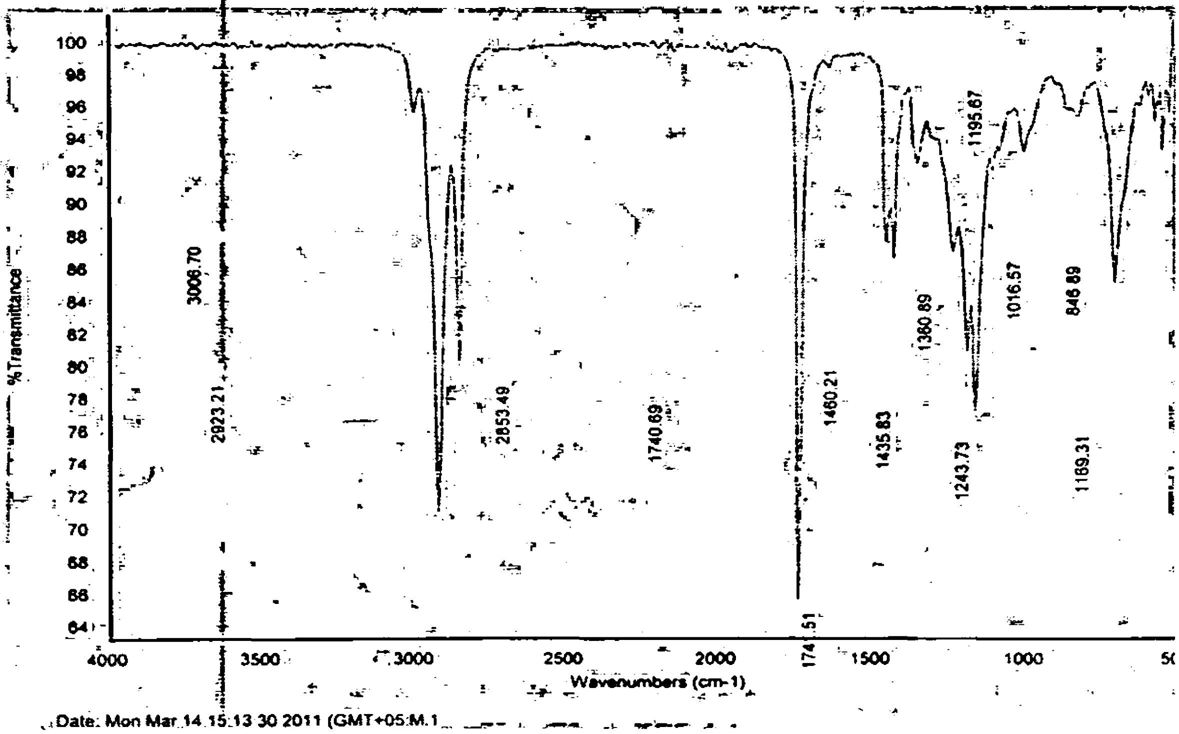


Figure 3.5: FT-IR spectra of biodiesel for molar ratio

The structure of fatty acids methyl esters (biodiesel) were elucidated by recording IR spectra of their respective peaks, various absorption bands are present in the table. The bands at the range of 1750-1730 can be associated to C=O and bands at the range of 1300-1000 can be attributed to C-O (asymmetric axial stretching). The bands at the range of 2980-2950 represents the CH3(s), while closely related bands at 2950-2850 are due to CH2 (s) and bands at 3050-3000 relates to CH (s). The band set 1475-1350 attributes to CH3 bending, bands at1350-1150 ascribed as CH2 bending and closely related band at 722 confirms CH bending. The FT-IR spectra of both waste cooking oil and biodiesel were same but the various differences should be observed for identification purposes. The shifting of absorption peaks of the oil at 1748, 1377, 1157 and 856 to 1742, 1361, 1168, 1015 and 878 in the biodiesel respectively. The disappearance of the peaks at 1465, 1095 and 964.4 from the spectra and appearance of new bands at 1435 and 1195 confirms the synthesis of biodiesel that was reported by Dennis et. Al (2008).It was concluded that by selecting an optimum range of temperature and molar ratio the results remains almost same.

3.3.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical chemistry technique used in quality control and research for determining the content and purity of a sample as well as its molecular structure. For example, NMR can quantitatively analyze mixtures containing known compounds. For unknown compounds, NMR can either be used to match against spectral libraries or to infer the basic structure directly. Once the basic structure is known, NMR can be used to determine molecular conformation in solution as well as studying physical properties at the molecular level such as conformational exchange, phase changes, solubility, and diffusion. In order to achieve the desired results, a variety of NMR techniques are available.

^{1}H NMR Data for Base-Catalyzed Trans-esterifies Biodiesel

1H NMR spectroscopy are useful tools for the confirmation of methyl esters and also to calculate the % conversion of triglycerides to corresponding methyl esters. The characteristic singlet peak of methoxy protons was observed at 2.24 ppm and a doublet of doublet of α CH2 proton at 1.93 ppm. These two peaks are the distinct peaks for the confirmation of methyl esters present in biodiesel. Terminal methyl proton peak at 0.810 ppm and intense signal of methylene protons of long chain of esters at 1.212 ppm was observed. A signal at 1.56 ppm corresponds to β-carbonyl methylene protons and at 5.254 ppm due to olefinic protons. Solvent peak of deuterated chloroform was observed at 7.289 ppm.

To compute the % age conversion of triglycerides to corresponding methyl esters, equation used was:

$$C = 100 \times 2A_{Me} / 3A_{CH2}$$

$$C = 100 \times 2(2.54)/3(1.93) \quad = 87.74$$

Where

C = percentage conversion of triglycerides to corresponding methyl esters

A_{Me} = integration value of the methoxy protons of the methyl esters and

A_{CH2} = integration value of α-methylene protons

By using the above equation, the percentage conversion of triglycerides to corresponding esters was found to be 87 % which is quite in good agreement with practically observed %.

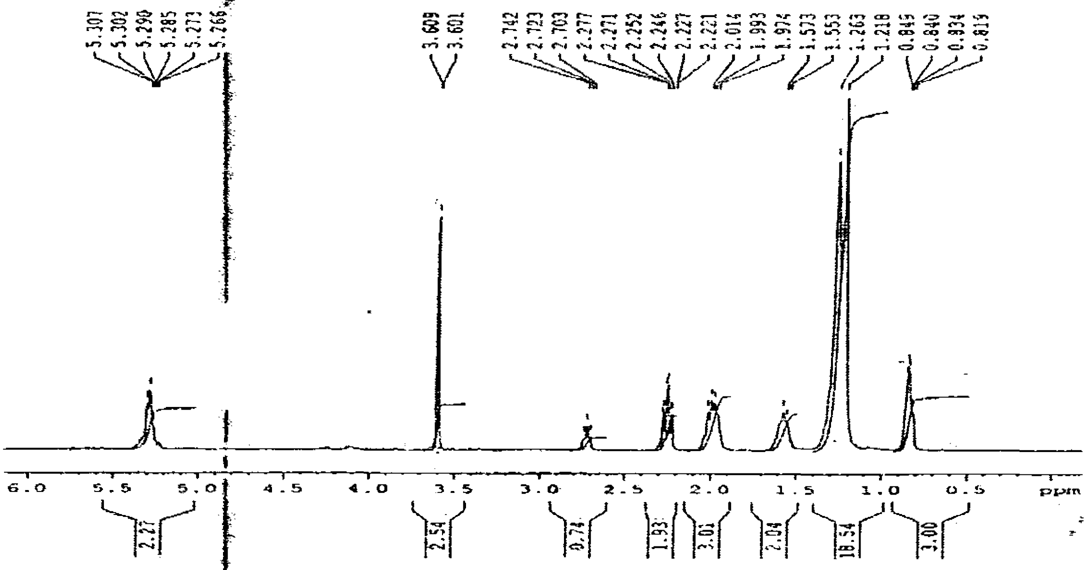


Figure 3.6: ^{1}H NMR of Biodiesel (temperature effect)

^{13}C NMR Data for Base-Catalyzed Trans-esterifies Biodiesel

The characteristic peaks of ester carbonyl (-COO-) and C-O at 174.01ppm and 51.22 ppm respectively was observed in the 13C NMR spectrum of the waste cooking oil biodiesel shown in figure 3.23. The peak around 127.82 ppm and 129.99 ppm confirms the olefinic bond in the methyl esters. The peaks in the range of 29.09-33.95 ppm are due to the methylene carbons of long carbon chain in fatty acid methyl esters. Solvent peak of deuterated chloroform was observed at 76.54-69 ppm.

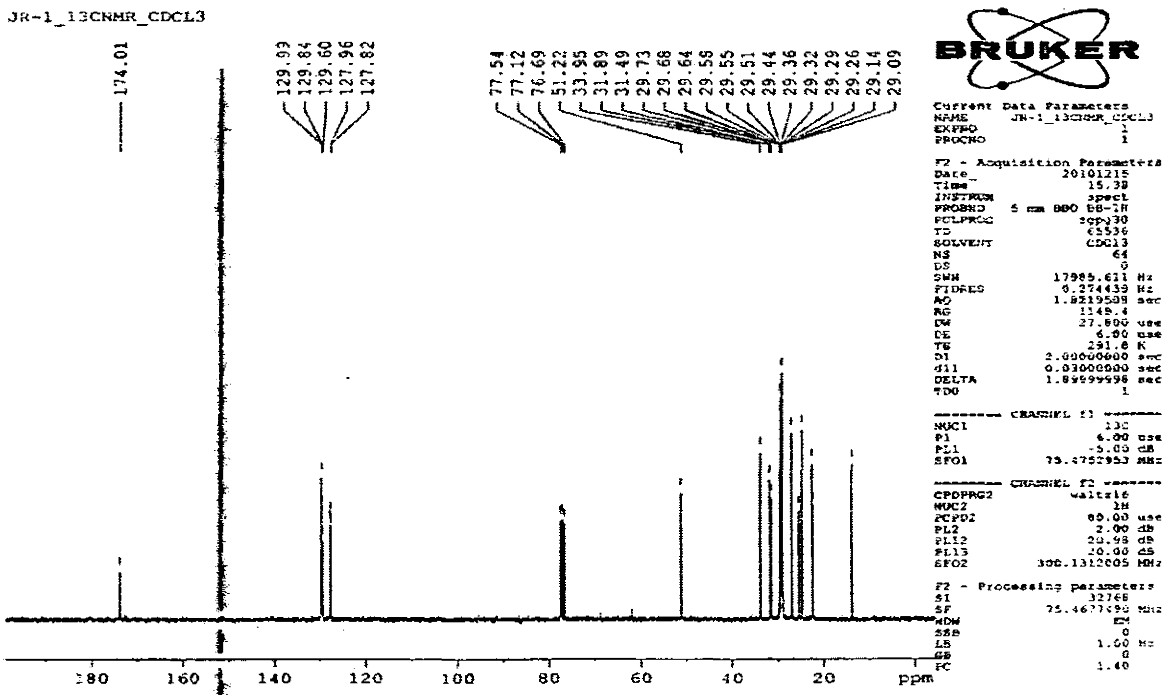


Figure 3.7: ^{13}C NMR studies of Biodiesel

3.3.3 Gas Chromatography / Mass Spectrometry (GC / MS):

Gas chromatography/mass spectrometry (GC/MS) is the synergistic combination of two powerful analytic techniques. The Gas chromatography/mass spectrometry (GC/MS) instrument separates chemical mixtures (the GC component). It is one of the most accurate tools for analyzing environmental samples. The GC works on the principle that the mixture will separated into individual substances when heated. The heated gases are carried through a column with an inert gas (such as helium). As the separated substances emerge from the column opening, they flow into the MS. Mass Spectrometry identifies compounds by the mass of analyte molecule. A "library" of known spectra, covering several thousand compounds, is stored on the computer. Mass spectrometry is considered the only definitive analytical detector.

Effect of Temperature

Table 3.4: Retention Time for Mass Spectra of Biodiesel

Sr. No	Fatty Acid corresponding Esters	Formula	Retention Time (min)
1.	Tetradecanoic acid. methyl ester	$CH_3(CH_2)_{13}COOCH_3$	9.790
2.	9- 11 Hexadedecanoic acid, methyl ester	$CH_3(CH_2)_5CH=CH(CH_2)_2COOCH_3$	10.763
3.	Hexadecanoic acid, methyl ester	$CH_3(CH_2)_{14}COOCH_3$	10.878
4.	10, 13-Octadecadienoic acid, methyl ester	$CH_3(CH_2)_3CH=CHCH_2CH=CH(CH_2)_8$ COOH	10.770
5.	Octadecenoic acid, methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	11.973
6.	11-Eicosenoic acid, methyl ester	$CH_2(CH_2)_7CH=CH(CH_2)_9COOCH_3$	12.635
7.	Eicosenoic acid, methyl ester	$CH_3(CH_2)_{18}COOCH_3$	11.743
8.	Docosanoic acid, methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOCH_3$	13.445
9.	Docosanoic acid, methyl ester	$CH_3(CH_2)_{20}COOCH_3$	13.527
10.	Tetracosenoic acid, methyl esters	$CH_3(CH_2)_7CH=CH(CH_2)_{13}COOCH_3$	14.310

Identification of Saturated Compounds

Distinguish peaks of higher saturated esters at $[M-31]^+$ due to α-cleavage (loss of methoxy group) and $[M-43]^+$ due to the removal of C_{2-4} propyl group was observed at all spectra of waste cooking oil methyl esters (WCOME) mass spectrum. Base peak of saturated WCOME's was observed at m/z = 74, which correspond to the McLafferty rearrangement. As a result of β-cleavage, the first member of cabomethoxy $[CH_3OOC\ (CH_2)\ n]^+$obtained at m/z = 87 where n=2, 3, 4, 5, 6…., m/z 87, 101, 115, 129, 143…, with difference of 14 a.m.u. due to the CH_2 unit, a hydrocarbon series of alkyl ions. McLafferty peak at m/z = 74, β-cleavage and alkyl series support our argument of saturated waste cooking oil methyl esters (WCOMEs). A representative mass spectrum of Eicosenoic acid methyl ester (C17:0) with mass fragmentation ions is shown in Figure 3.8.

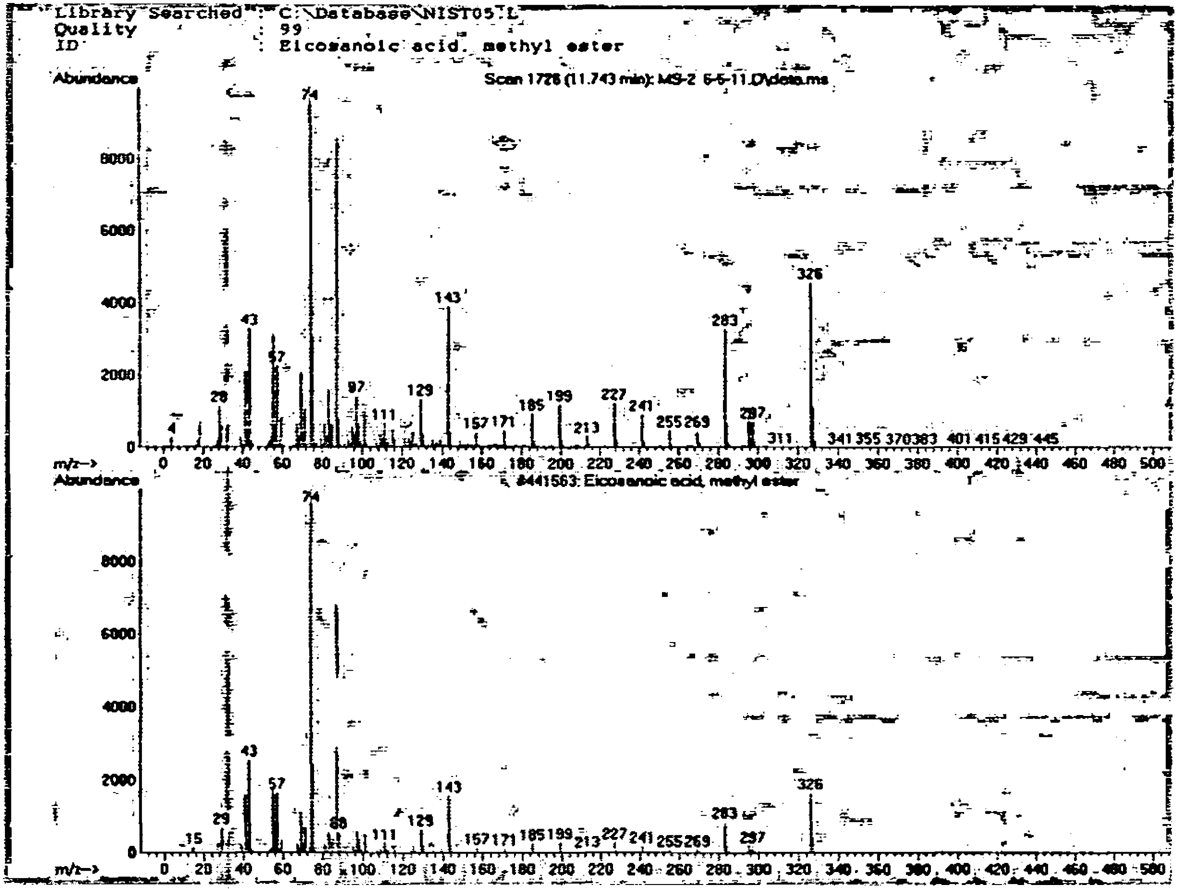
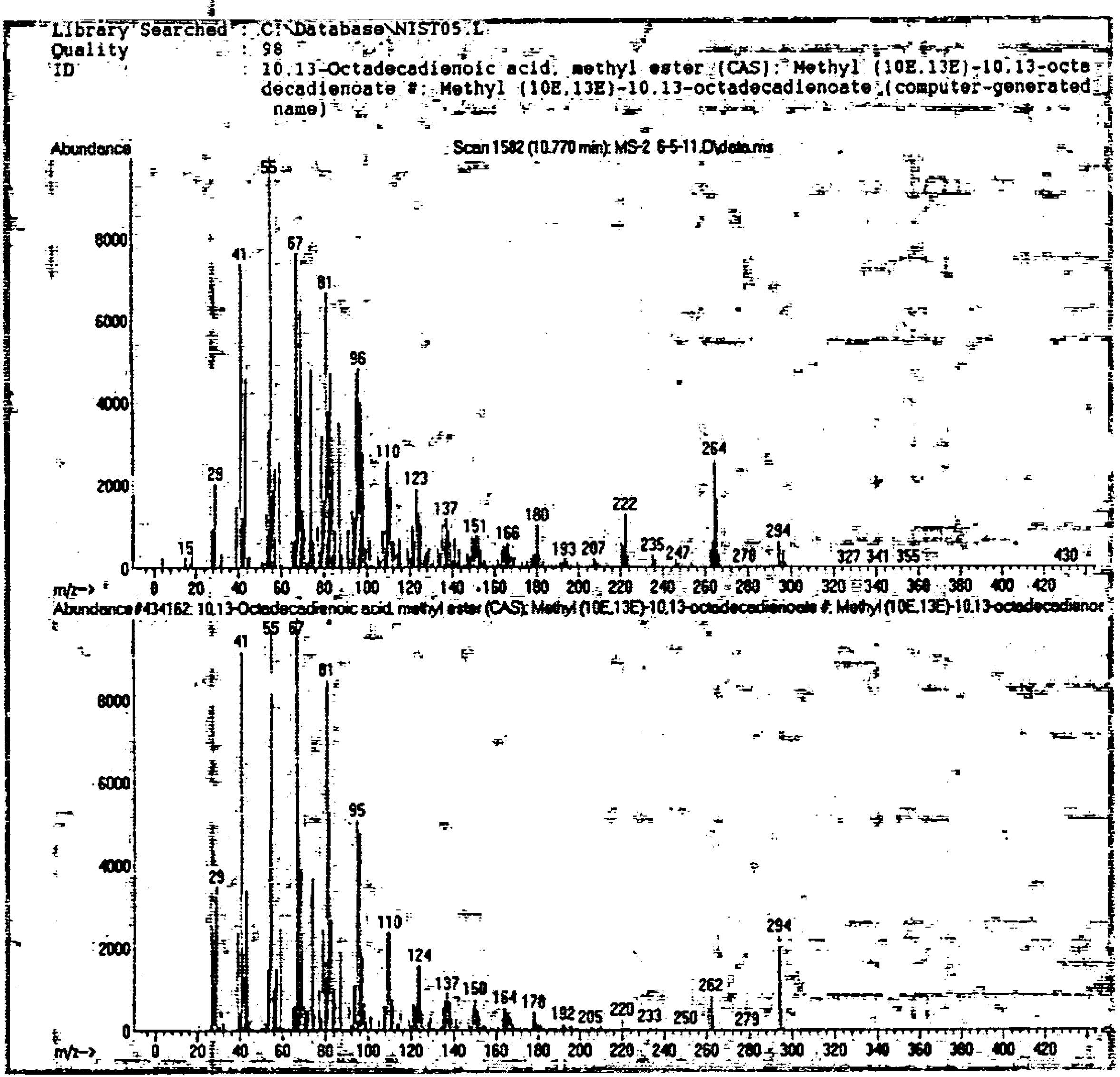


Figure 3.8: MS spectra of Saturated Compounds

Identification of Unsaturated Compounds

10, 13- Octadecadienoic acid methyl ester, is the diunsaturated methyl esters observed in the GC of the waste cooking oil biodiesel. 10, 13-octadecadienoate methyl ester (C18:2) fragmentation showed a characteristic base peak at m/z 55, $[M-31]^+$ due to loss of methoxy group and McLafferty rearrangement peak at m/z =74. Hydrocarbon ions $[CnH2n - 3]^+$ were seen in the lower mass range at m/z 67, 81, 95, 109, 123,137 etc. A representative mass spectrum of 10, 13-Octadecadienoic acid methyl ester (C18:2) with mass fragmentation ions is shown in Figure 3.9.



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                    name)
```

Figure 3.9: MS spectra of Unsaturated Compounds

3.3.3 (II) Effect of Molar Ratio

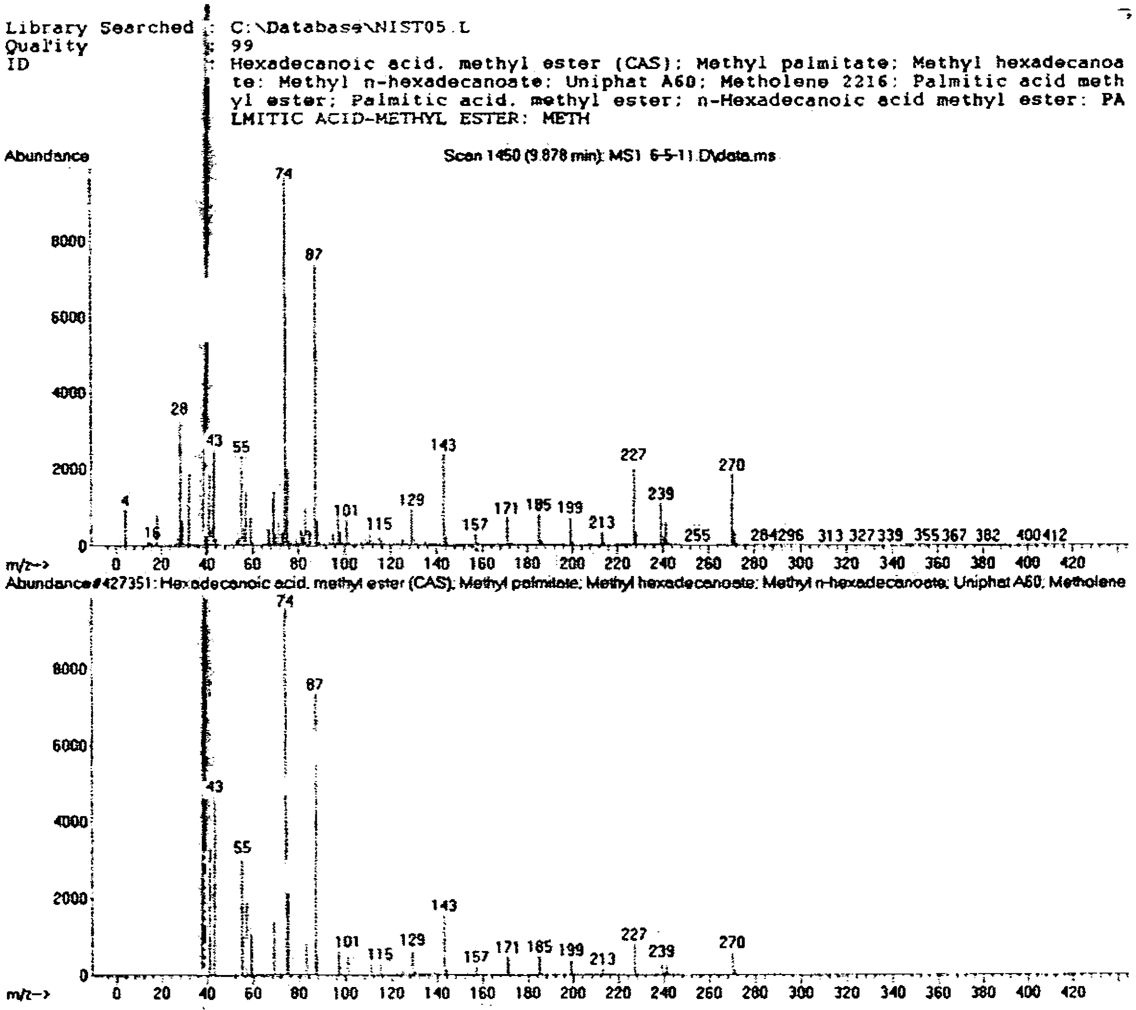
For the effect of molar ration of sodium hydroxide following results were obtained:

Table 3.5: Retention Time for Mass Spectra of Biodiesel

S.No	FattyAcid corresponding Esters	Formula	Retention Time (min)
1.	Tetradecanoic acid. methyl ester	$CH_3(CH_2)_{13}COOCH_3$	8.797
2.	9-11 Hexadedecanoic acid, methyl ester	$CH_3(CH_2)_3CH=CH(CH_2)_2COOCH_3$	9.763
3.	Hexadecanoic acid, methyl ester	$CH_3(CH_2)_{14}COOCH_3$	9.878
4.	10, 13-Octadecadienoic acid, methyl ester	$CH_3(CH_2)_3CH=CHCH_2CH=CH(CH_2)_8COOH$	10.729
5.	Octadecenoic acid, methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	10.927
6.	11-12 Eicosenoic acid, methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_5COOCH_3$	11.635
7.	Eicosenoic acid, methyl ester	$CH_3(CH_2)_{18}COOCH_3$	11.723
8.	Docosanoic acid, methyl ester	$CH_3(CH_2)_{20}COOCH_3$	12.527
9.	15-17 Tetracosenoic acid, methyl esters	$CH_3(CH_2)_7CH=CH(CH_2)_{13}COOCH_3$	13.324
10.	Oleic acid, methyl esters	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	14.128

Identification of Saturated Compounds

Distinguish peaks of higher saturated esters at $[M-31]^+$ due to α-cleavage (loss of methoxy group) and $[M-43]^+$ due to the removal of C_{2-4} propyl group was observed at all spectra of waste cooking oil methyl esters (WCOME) mass spectrum. Base peak of saturated WCOME's was observed at m/z = 74, which correspond to the McLafferty rearrangement. As a result of β-cleavage, the first member of cabomethoxy $[CH_3OOC\ (CH_2)\ n]^+$obtained at m/z = 87 where n=2, 3, 4, 5, 6…., m/z 87, 101, 115, 129, 143…, with difference of 14 a.m.u. due to the CH_2 unit, a hydrocarbon series of alkyl ions. McLafferty peak at m/z = 74, β-cleavage and alkyl series support our argument of saturated waste cooking oil methyl esters (WCOMEs). A representative mass spectrum of Hexadecanoic acid methyl ester (C20:0) with mass fragmentation ions is shown in Figure 3.10.



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                   LMITIC ACID-METHYL ESTER: METH
```

Figure 3.10: MS spectra for Saturated Compound

Identification of Unsaturated Compounds

10, 13- Octadecadienoic acid methyl ester, are the three diunsaturated methyl esters observed in the GC of the waste cooking oil biodiesel. 10, 13-octadecadienoate methyl ester (C18:2) fragmentation showed a characteristic base peak at m/z 41, $[M-31]^+$ due to loss of methoxy group and McLafferty rearrangement peak at m/z =55. Hydrocarbon ions $[CnH2n - 3]^+$ were seen in the lower mass range at m/z 67, 81, 95, 109, 123,137 etc. A representative mass spectrum of 10, 13-Octadecadienoic acid methyl ester (C18:2) with mass fragmentation ions is shown in Figure 3.11.

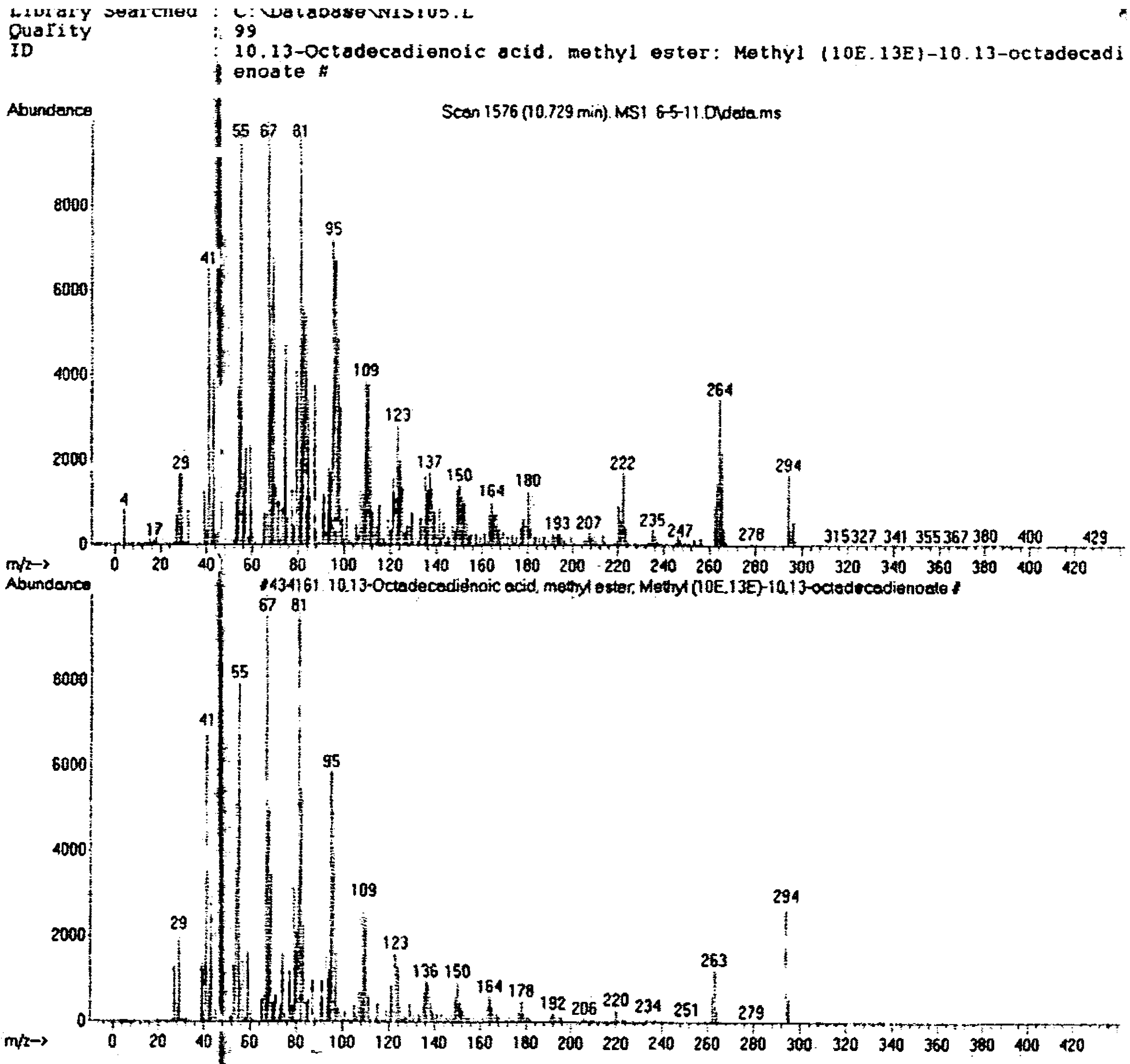

Figure 3.11: MS spectra of Unsaturated Compounds

3.4 Biodiesel production By Nano Catalysts:

The conventional industrial production of biodiesel is through transesterification of crude oil with a homogeneous strong base catalyst such as NaOH and KOH was studied previously. After reaction, recovery of glycerol, removal of base catalyst from products, and treatment of alkaline wastewater are costly and non-environmental. Furthermore, a homogeneous base catalyst is ineffective for production biodiesel from high acid-value crude oils due to the formation of soap. Tan et al. reported a catalyst-free biodiesel production method, using waste palm cooking oil as raw material and supercritical methanol. But the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1). Therefore, heterogeneous solid catalysts were used for the transesterification process, where a better separation and reuse of the catalysts without saponification were achieved. Preparation and application of solid superbase catalysts are an emerging area that is attracting more and more attention, because the catalysts are easily separated for reuse and possess a high activity for various reactions under mild conditions. They can replace homogeneous base catalysts in order to minimize the production of pollutants. For this purpose nano catalysts of cobalt oxide, nickel oxide, copper-cerium oxide and copper-nickel oxide were synthesized for the conversion of waste cooking oil into biodiesel and then the results were compared with conventional process.

3.5 Characterization of Nano Particles:

In this particular research work, various techniques like XRD, SEM,BET were used to characterize the nano-catalysts which were employed for the production of biodiesel.

The results of these techniques are interpreted and discussed one by one below.

3.5.1 X-ray Diffraction Spectroscopy (XRD)

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of poly crystals, defects, stresses, etc.

The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. XRD is nondestructive and does not require elaborate sample preparation, which partly explains the wide usage of XRD method in materials characterization.

If there is no inhomogeneous strain, the crystallite size, D, can be estimated from the peak width with the Scherrer's formula.

$$\mathbf{Dp = 57.3K\lambda\ /B\ \cos\theta}$$

Where λ is the X-ray wavelength, B is the full width of height maximum (FWHM) of a diffraction peak, θ is the diffraction angle, and K is the Scherrer's constant of the order of unity for usual crystal. However, one should be alerted to the fact that nanoparticles often form twinned structures; therefore, Scherrer's formula may produce results different from the true particle sizes. In addition, X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizable amount of powder. It should be noted that since the estimation would work only for very small particles, this technique is very useful in characterizing nanoparticles. Typical intensities for electron diffraction are 108 times larger than for XRD. Because of small diffraction intensities, XRD generally requires large specimens and the information acquired is an average over a large amount of material.

Following are the XRD patterns of nano catalysts:

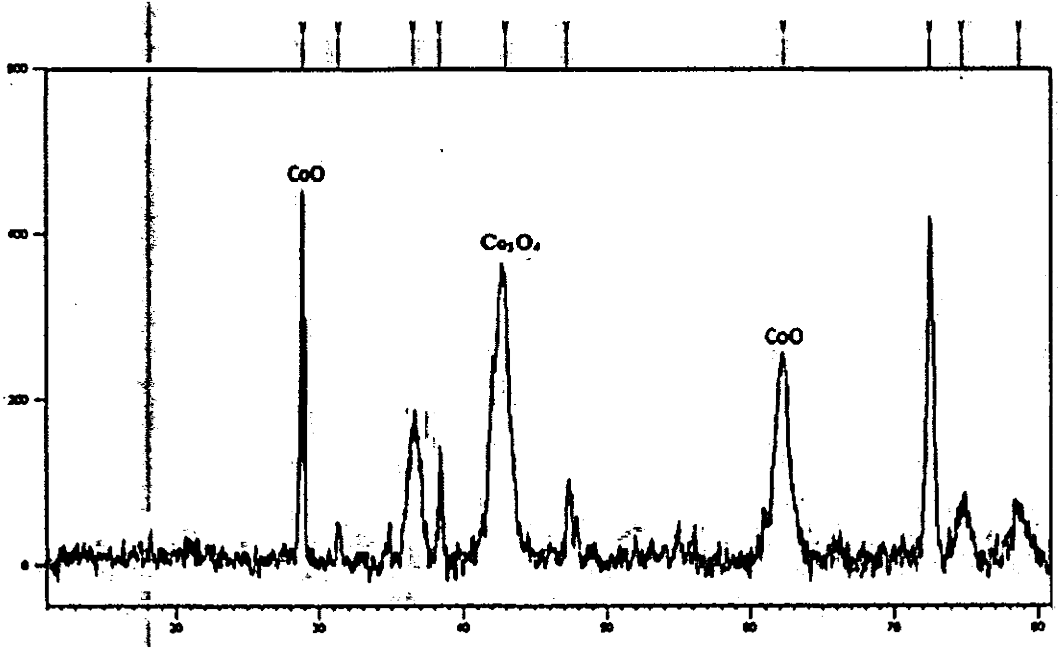

Figure 3.12: XRD Spectrum for Cobalt Nano Catalyst

The peaks obtained for cobalt nano particles at 2 θ position on 37 corresponds to cobalt oxide (Ref: ICDD 75-0393), peaks at 58 and 64 corresponds to cobalt oxide (ref: 80-1540), no extra peaks appeared in the spectra and it could be concluded that the nanoparticles of cobalt prepared through this method were pure with a controlled particle size having no impurities.

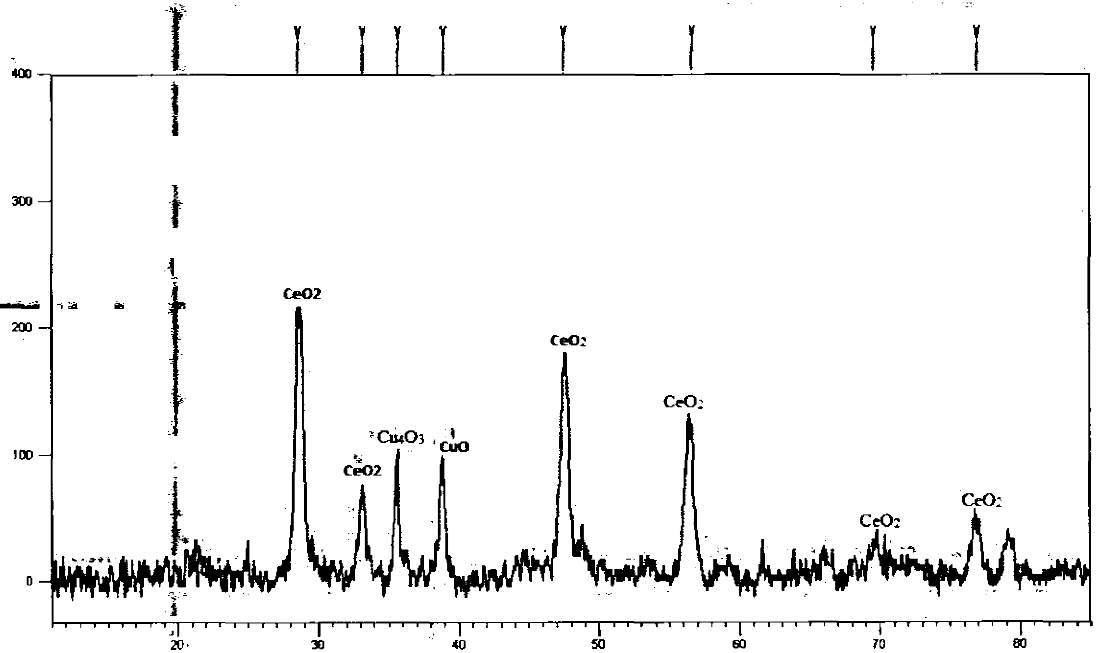

Figure 3.13: XRD Spectrum for Copper-Cerium Nano Catalyst

The peaks obtained for cerium-copper nanoparticles at 2 θ position on 29 and 33 corresponds to cerium oxide (ICDD-75-0076), peak at 35 corresponds to paramelaconite (ICDD-83-1665), peak at 39 corresponds to teronite (ICDD-02-1040),peaks at 48, 57 corresponds to cerianite.syn (ICDD-43-1002), peaks at 70 corresponds to cerium oxide (ICDD-75-0076) and peak at 77 corresponds to cerianite.syn (ICDD-43-1002) respectively no extra peaks appeared in the spectra and it could be concluded that the nanoparticles of cerium-copper prepared through this method were pure with a controlled particle size having no impurities.

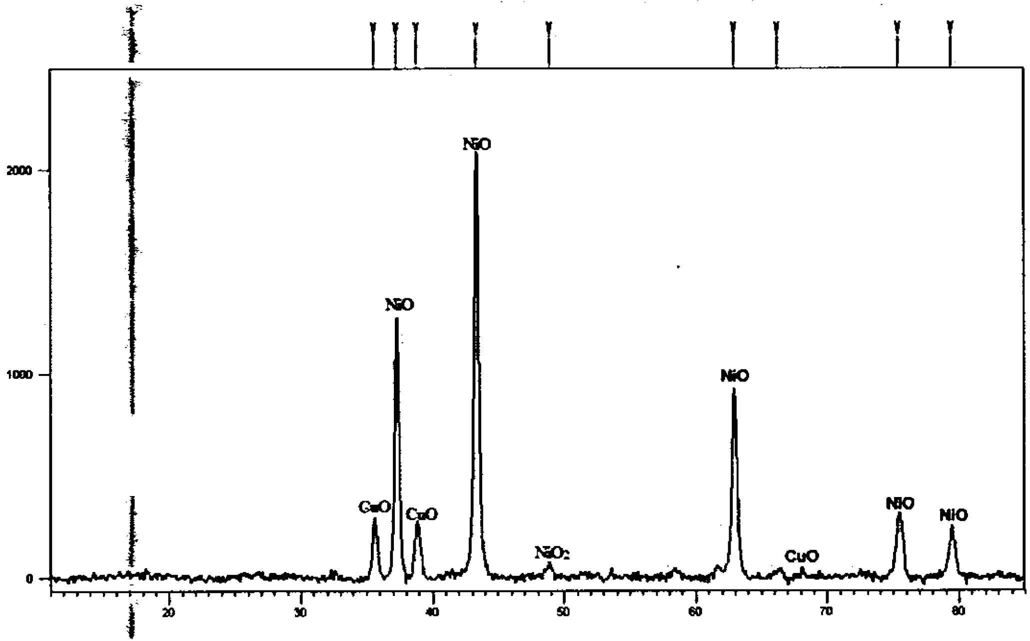

Figure 3.14: XRD Spectrum for Copper-Cerium Nano Catalyst

The peaks obtained for copper-nickel oxide nanoparticles at $2\theta = 35$ corresponds to teronite. syn (ICDD-05-0661), $2\theta = 36$ corresponds to bunsinite. syn (ICDD-04-0835), $2\theta = 39$ corresponds to teronite.syn (ICDD-05-0661), $2\theta = 43{,}48$ corresponds to nickel oxide (ICDD-85-1977), $2\theta = 62$ corresponds to bunsinite. syn (ICDD-04-0835), $2\theta = 68$ corresponds to teronite (ICDD-03-0884), $2\theta = 74$ and 78 corresponds to bunsenite.syn (ICDD-04-0835),no extra peaks appeared in the spectra and it could be concluded that the nanoparticles of copper- nickel oxide prepared through this method were under controlled particle size having no impurities.

The size of particles was estimated based on the half with of the diffraction peaks using following formula.

$$\mathbf{D = 57.3\ K\ \lambda / \beta \cos \theta}$$

Where D = Particle size of the catalyst in °A units

K = 0.9

λ = Wavelength of source radiation in °A units

0 = Peak position

β = Full width half maximum (FWHM)

Table 3.6: Particle Size Calculated from XRD Data

Sr.No.	Particle Name	Size(nm)
1	CoO	**38**
2	Cu_2O-CeO	**17**
3	Cu_2O-NiO	**8**

XRD analysis gave information about phase and size of the particle through Scherrer's formula. XRD has given prominent peaks for the metallic nanoparticles of cerium-copper and copper-nickel.

3.5.2 Scanning Electron Microscopy (SEM)

SEM is one of the most widely used techniques used in characterization of nanomaterials and nanostructures. SEM enables the imaging of the topography of solid surface by use of back scattered on secondary electrons. With the help of SEM micrographs, we get the information about dispersion of metals, interaction of metals with supported and morphology of surface.

The following figures show the SEM of the fresh metallic oxide nano catalysts.

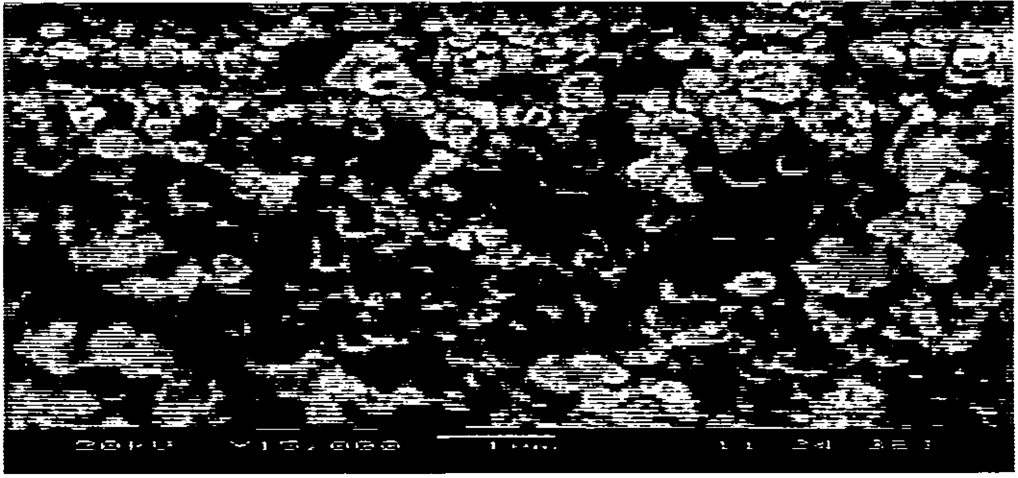

Figure 3.15: SEM of cobalt oxide nano particles

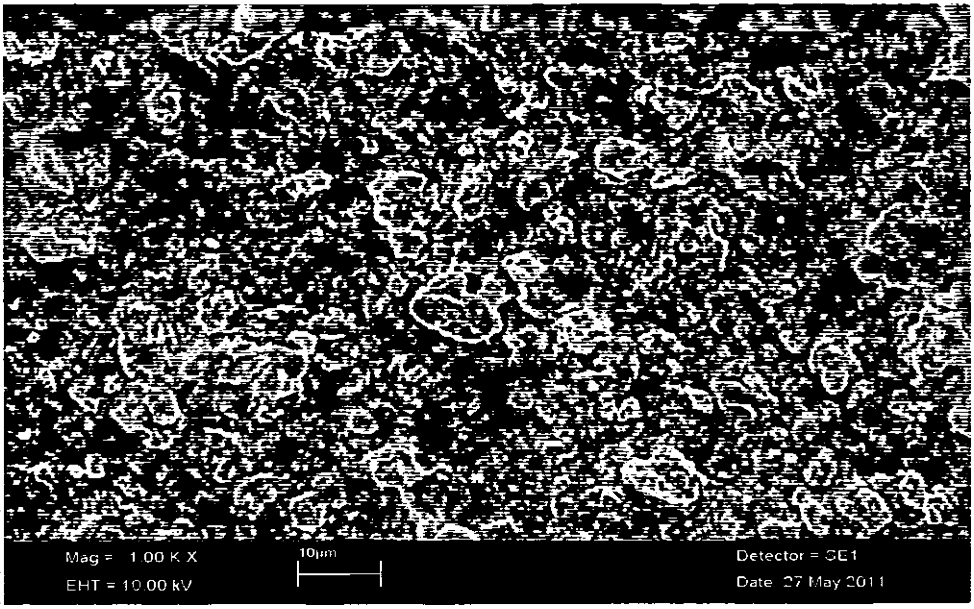

Figure 3.16: SEM of nickel oxide nano particles

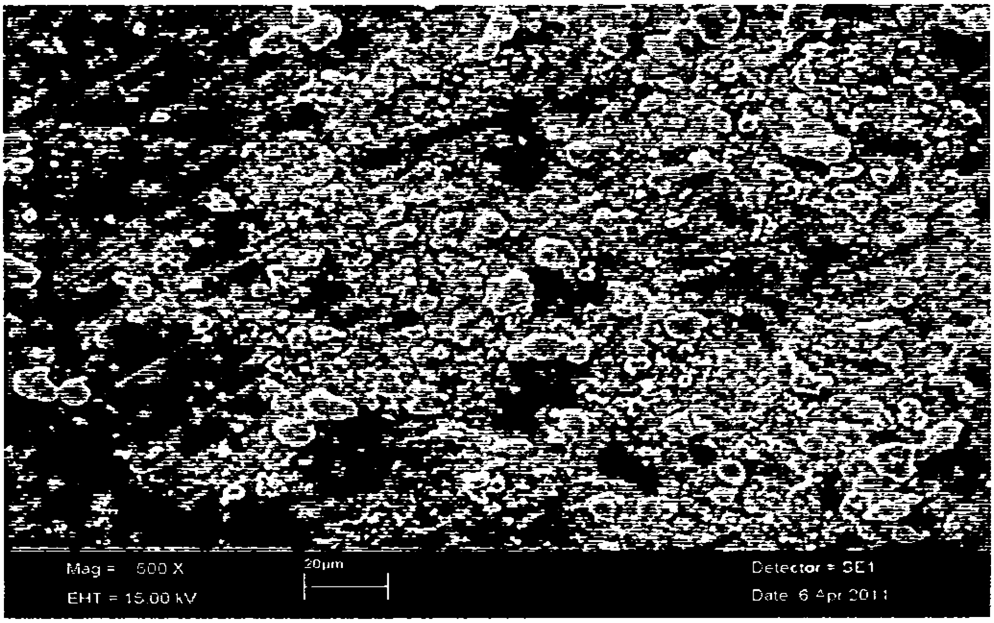

Figure 3.17: SEM of Copper Cerium oxide Nano Composites

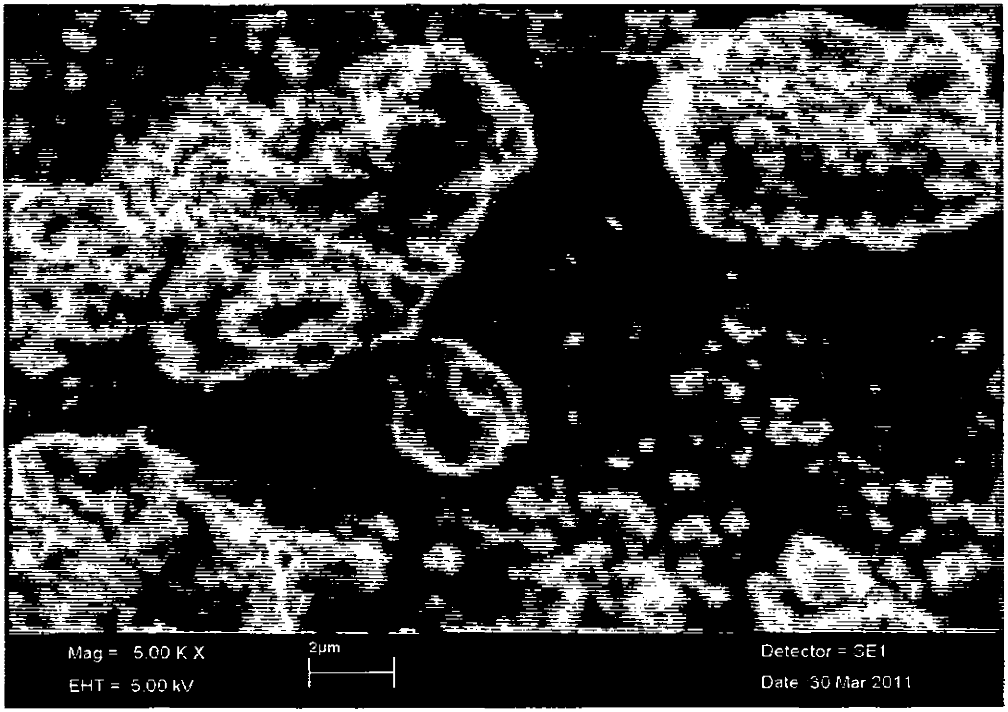

Figure 3.18: SEM of Copper Nickel oxide Nano Composites

The metallic nano catalysts synthesized through co precipitation method were analyzed for their morphology through SEM. SEM analysis of fresh samples indicates that metallic species are uniformly distributed over the supported and particles of cobalt oxide are spherical in shape figure 3.15 and figure 3.16 indicates that nickel oxide nano particles are random in shape. Figure 3.17 above shows the SEM image of copper-cerium oxide nano composites and figure 3.18 corresponds to copper-cerium oxide nano catalysts. This indicates that the catalysts are spherical in shape. Moreover the particles of copper –nickel composites are also spherical in shape as shown in figure 3.17. All the above mentioned particles are uniformly distributed which supported the superiority of our synthesis procedures.

3.5.3 Energy Dispersive X-ray Analysis (EDX)

Energy dispersive X-ray analysis (EDX) is the standard method for obtaining chemical analysis in specimens being examined in electron microscopes. In electron microscopes X-rays are emitted as the electron beam interacts with the material being examined. Each atomic element has discrete characteristic energies for the X-rays providing a basis for chemical analysis. This technique is used in conjunction with SEM and is not a surface science technique.

Table 3.7: Comparison of the actual composition of the catalysts and EDX results

Sr. No.	Metals	% Composition	Actual % Composition
1.	Cobalt	67.4	66
2.	Nickel	46	48.2
3.	Copper-Cerium	72	73
4.	Copper-Nickel	78.5	81

3.5.4 Brunauer Emmett and Teller Instrument Analysis (BET)

BET analysis was used to determine the surface area of the catalyst materials [115-117]. It is known that BET surface area has no effect on the phase of the nano particles [115]. But they do have an effect on the reactivity of nano particles. Large surface area has increased adsorption/desorption capacity, consequently good photo catalytic activity. The small particle size has a large surface /volume ratio and large pore volume. Table presents the measured surface area of the prepared cobalt, nickel, copper cerium and copper nickel nano catalysts.

Table 3.8: BET surface area measurement

Sr .No	Catalysts	BET Surface area (m^2g^{-1})
1.	Cobalt oxide	97
2.	Nickel oxide	89
3.	Copper-Cerium oxide	130
4.	Copper-Nickel oxide	110

3.6 Characterization of Nano Catalyzed Biodiesel

Various experiments were performed by using nano catalysts but the most optimal results were shown by copper-cerium and copper-nickel catalysts. Biodiesel production was confirmed by using techniques like NMR, FTIR and GC/MS which ensured that 80% of fatty acids in waste cooking oil were converted into methyl esters without the formation of any by-products.

3.6.1 Fourier Transform Infrared Spectroscopy (FT-IR):

FT-IR of most optimal results of biodiesel using copper-cerium and copper-nickel nano composites were:

Table 3.9: FT-IR studies of Nanocatalyzed Biodiesel

Sr. No	Functional Group	Observed Frequency	
		Cu-Ce	Cu-Ni
1.	C=O	1748.97	1748.97
2.	C-O	1195.67	1195.67
3	CH_2	2915.86 2846.66	2915.86 2846.66
4.	CH (stretching)	3006.90	3006.90
5.	CH_3 (bending)	1467.59	1467.59
6.	CH_2 (bending)	1169.66	1169.66
7.	CH (bending)	722.76	722.76

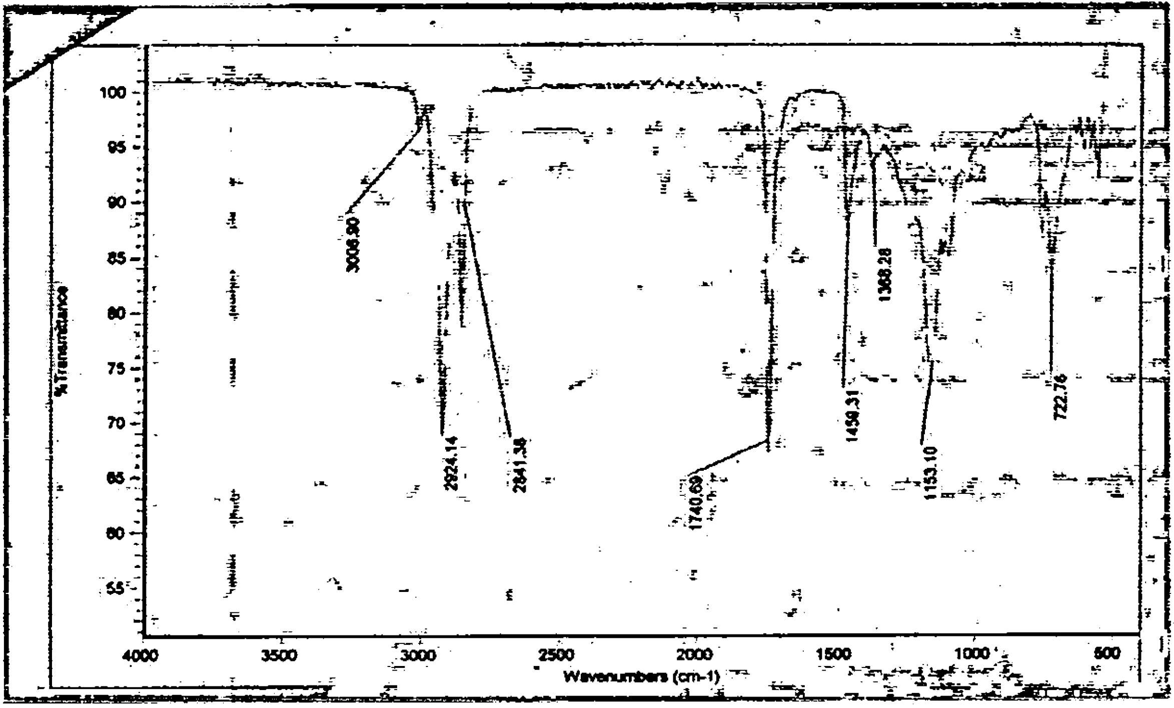

Figure 3.19: FT-IR of Cu_2O-CeO

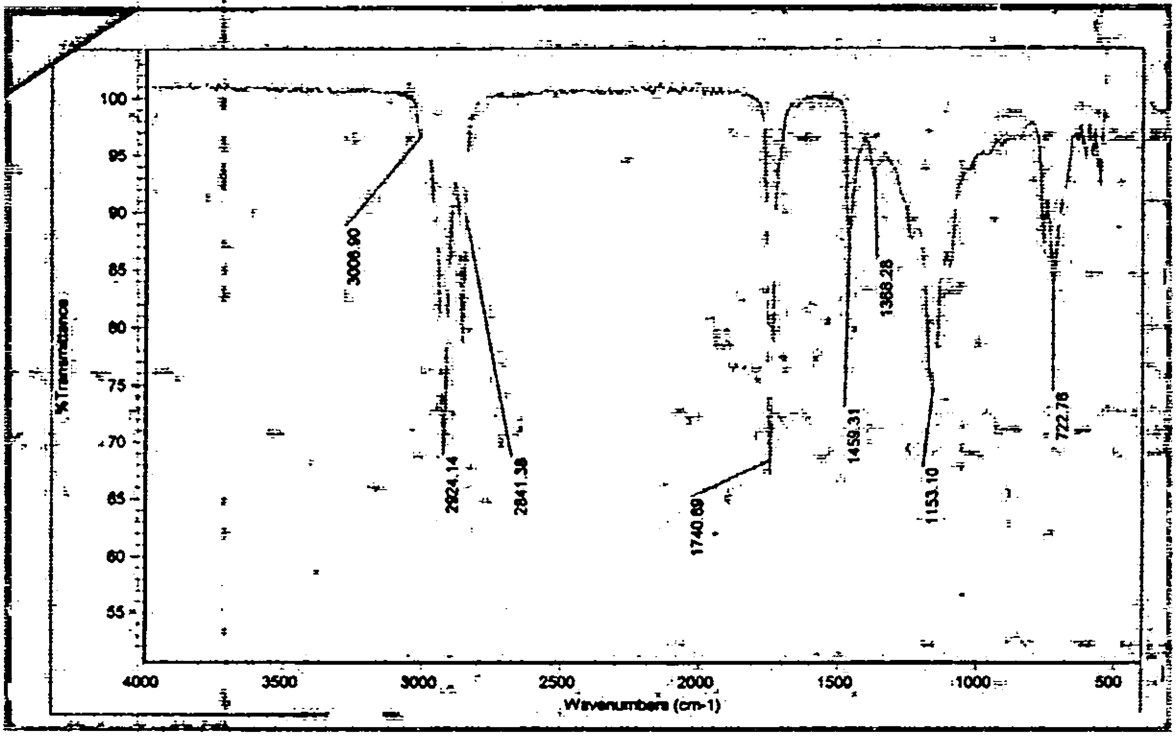

Figure 3.20: FT-IR of Cu_2O-NiO

The structure of fatty acids methyl esters (biodiesel) were elucidated by recording IR spectra of their respective peaks, various absorption bands are present in the table. The bands at the range of 1750-1730 can be associated to C=O and bands at the range of 1300-1000 can be attributed to C-O (asymmetric axial stretching). The bands at the range of 2980-2950 represents the CH3(s), while closely related bands at 2950-2850 are due to CH2 (s) and bands at 3050-3000 relates to CH (s). The band set 1475-1350 attributes to CH3 bending, bands at1350-1150 ascribed as CH2 bending and closely related band at 722 confirms CH bending. The FT-IR spectra of both waste cooking oil and biodiesel were same but the various differences should be observed for identification purposes. The shifting of absorption peaks of the oil at 1748, 1377, 1157 and 856 to 1742, 1361, 1168, 1015 and 878 in the biodiesel respectively. The disappearance of the peaks at 1465, 1095 and 964.4 from the spectra and appearance of new bands at 1435 and 1195 confirms the synthesis of biodiesel that was reported by Dennis et. Al (2008).

3.6.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

For the NMR studies of copper-nickel oxide and copper-cerium oxide biodiesel:

^{1}H NMR Data for Cu_2O/NiO Nano-Catalyzed Trans-esterifies Biodiesel

^{1}H NMR spectroscopy are useful tools for the confirmation of methyl esters and also to calculate the % conversion of triglycerides to corresponding methyl esters. The characteristic singlet peak of methoxy protons was observed at 2.71 ppm and a doublet of doublet of α CH2 proton at 1.88 ppm. These two peaks are the distinct peaks for the confirmation of methyl esters present in biodiesel. Terminal methyl proton peak at 0.810 ppm and intense signal of methylene protons of long chain of esters at 1.212 ppm was observed. A signal at 1.56 ppm corresponds to β-carbonyl methylene protons and at 5.254 ppm due to olefinic protons. Solvent peak of deuterated chloroform was observed at 7.289 ppm.

To compute the %age conversion of triglycerides to corresponding methyl esters, equation used was:

$$C = 100 \times \frac{2(2.71)}{3(1.88)} = 96.09\ \%$$

Where

C = percentage conversion of triglycerides to corresponding methyl esters

A_{Me} = integration value of the methoxy protons of the methyl esters and

A_{CH2} = integration value of α-methylene protons

By using the above equation, the percentage conversion of triglycerides to corresponding esters was found to be 87 % which is quite in good agreement with practically observed %.

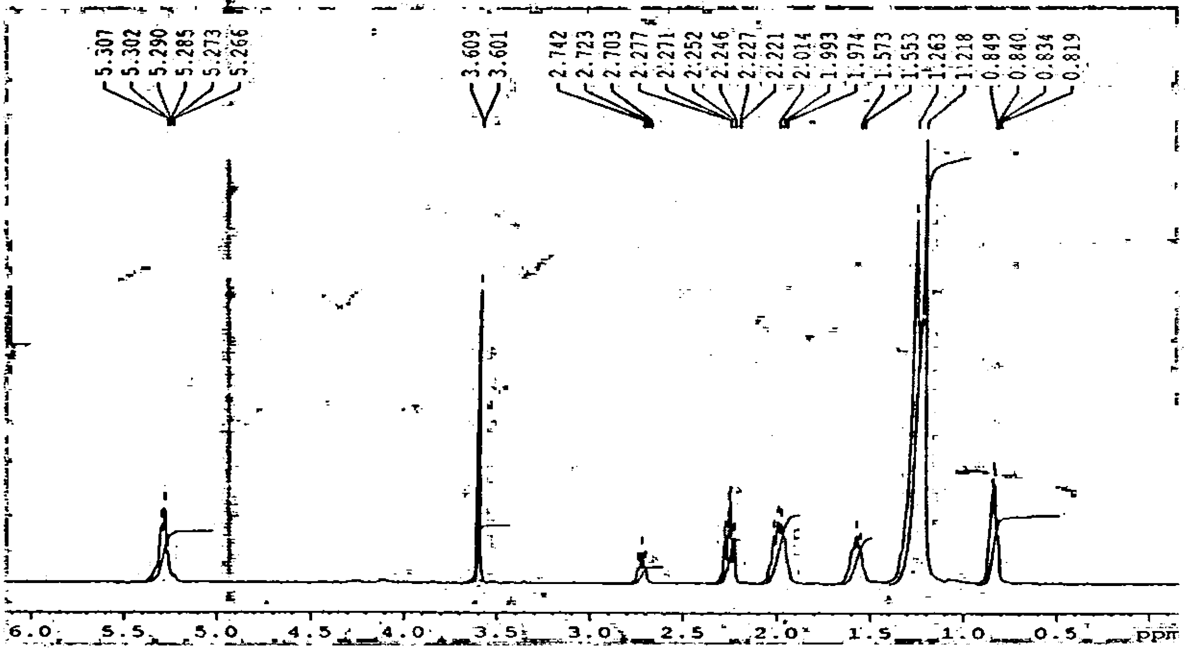

Figure 3.21: ^1H NMR of Cu_2O/NiO Nanocatalyzed Biodiesel

^{13}C NMR Data for Nano-Catalyzed Trans-esterifies Biodiesel

The characteristic peaks of ester carbonyl (-COO-) and C-O at 174.01ppm and 51.22 ppm respectively was observed in the ^{13}C NMR spectrum of the waste cooking oil biodiesel shown in figure 3.19. The peak around 127.82 ppm and 129.99 ppm confirms the olefinic bond in the methyl esters. The peaks in the range of 29.09-33.95 ppm are due to the methylene carbons of long carbon chain in fatty acid methyl esters. Solvent peak of deuterated chloroform was observed at 76.54-69 ppm.

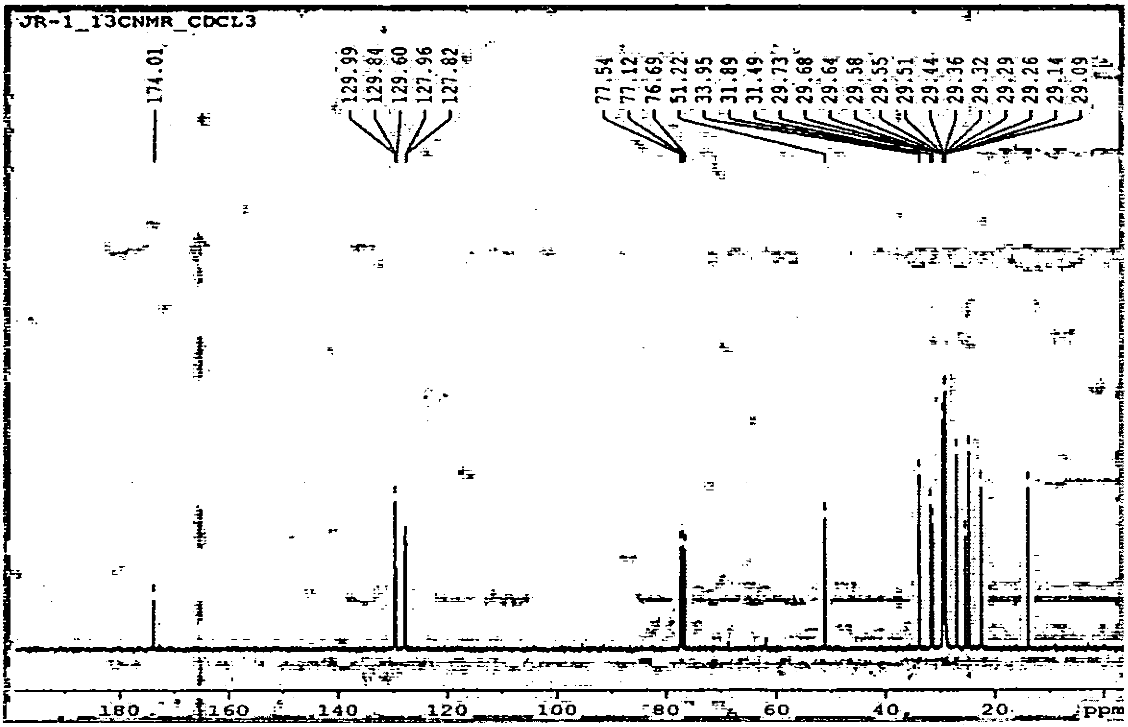

Figure 3.22: ^{13}C NMR of Cu_2O/NiO Nanocatalyzed Biodiesel

Investigation of Cu-Ce Nano Catalyzed Biodiesel by NMR

For the biodiesel synthesis by Cu-Ce nano composite NMR studies revealed that:

^{1}H NMR Studies:

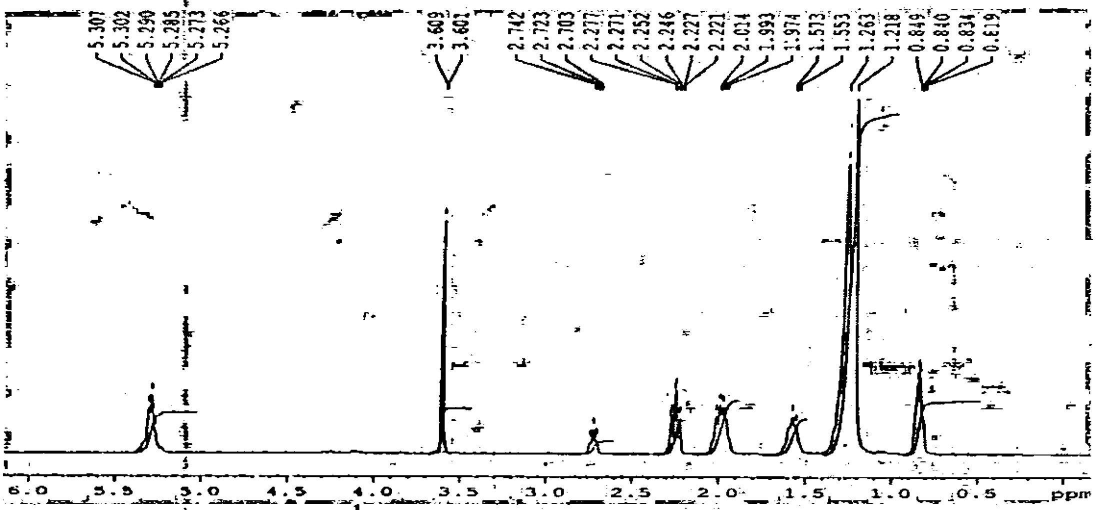

Figure 3.23: ^{1}H NMR of Cu_2O-CeO Nanocatalyzed Biodiesel

^{1}H NMR spectroscopy is useful tools for the confirmation of methyl esters and also to calculate the % conversion of triglycerides to corresponding methyl esters. The characteristic singlet peak of methoxy protons was observed at 2.24 ppm and a doublet of doublet of α CH2 proton at 1.93 ppm. These two peaks are the distinct peaks for the confirmation of methyl esters present in biodiesel. Terminal methyl proton peak at 0.810 ppm and intense signal of methylene protons of long chain of esters at 1.212 ppm was observed. A signal at 1.56 ppm corresponds to β-carbonyl methylene protons and at 5.254 ppm due to olefinic protons. Solvent peak of deuterated chloroform was observed at 7.289 ppm.

To compute the % age conversion of triglycerides to corresponding methyl esters, equation used was:

was:

$$C = 100 \times \frac{2(2.81)}{3(1.88)} = 97.09\ \%$$

Where

C = percentage conversion of triglycerides to corresponding methyl esters

A_{Me} = integration value of the methoxy protons of the methyl esters and

A_{CH2} = integration value of α-methylene protons

By using the above equation, the percentage conversion of triglycerides to corresponding esters was found to be 87% which is quite in good agreement with practically observed %.

^{13}C NMR Studies:

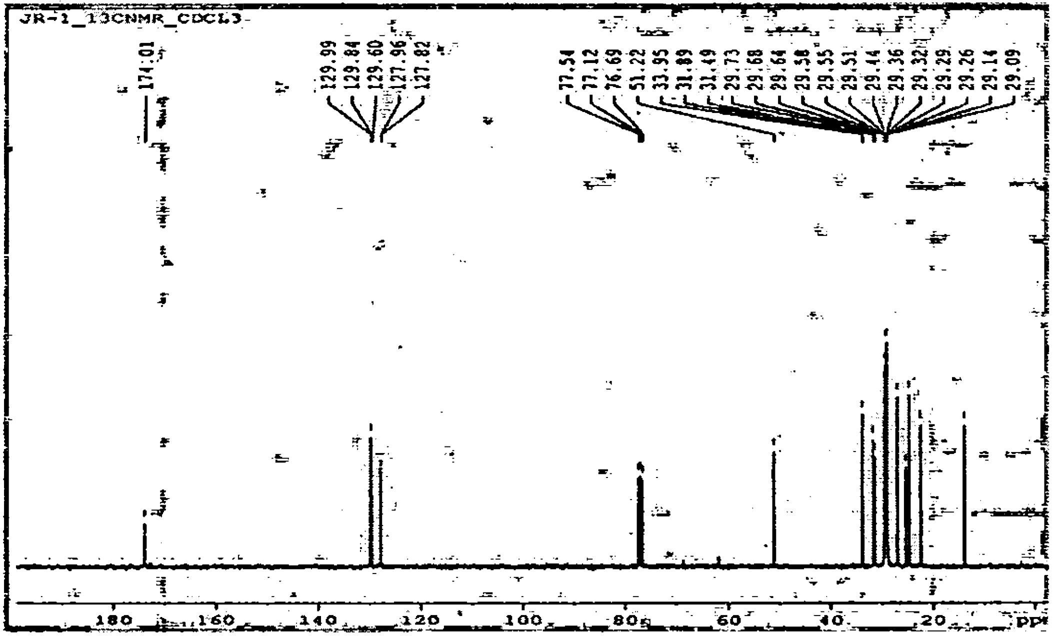

Figure 3.24: ^{13}C NMR studies of Cu_2O-CeO Biodiesel

The characteristic peaks of ester carbonyl (-COO-) and C-O at 174.01ppm and 51.22 ppm respectively was observed in the ^{13}C NMR spectrum of the waste cooking oil biodiesel shown in figure 3.21. The peak around 127.82 ppm and 129.99 ppm confirms the olefinic bond in the methyl esters. The peaks in the range of 29.09-33.95 ppm are due to the methylene carbons of long carbon chain in fatty acid methyl esters. Solvent peak of deuterated chloroform was observed at 76.54-69 ppm.

3.6.3 Gas Chromatography / Mass Spectrometry (GC / MS)

Several experiments were conducted using nano catalysts for conversion of waste cooking oil into biodiesel but the best results were obtained by two catalysts i.e. Cu-Ce and Cu-Ni nano composites under optimal conditions.

Identification of Cu_2O-CeO Nano Catalyzed Biodiesel

Table 3.10: Retention Time for MS spectra of biodiesel

Sr.No	Fatty Acid corresponding Esters	Formula	Retention Time (min)
1.	Tetradecanoic acid. methyl ester	$CH_3(CH_2)_{13}COOCH_3$	8.797
2.	9- Hexadedecanoic acid, methyl ester	$CH_3(CH_2)_5CH{=}CH(CH_2)_2COOCH_3$	9.763
3.	Hexadecanoic acid, methyl ester	$CH_3(CH_2)_{14}COOCH_3$	9.878
4.	10, 13-Octadecadienoic acid, methyl ester	$CH_3(CH_2)_3CH{=}CHCH_2CH{=}CH(CH_2)_8COOH$	10.729
5.	9-Octadecenoic acid, methyl ester	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	10.927
6.	11-Eicosenoic acid, methyl ester	$CH_2(CH_2)_7CH{=}CH(CH_2)_9COOCH_3$	11.635
7.	Eicosenoic acid, methyl ester	$CH_3(CH_2)_{18}COOCH_3$	11.723
8.	4- (o-methylphenyl 11)-2, 6-diphenylpyridine		12.452
9.	Docosanoic acid, methyl ester	$CH_3(CH_2)_{20}COOCH_3$	12.527
10.	15- Tetracosenoic acid, methyl esters	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOCH_3$	13.324
11.	Oleic acid, methyl esters	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	14.128

Investigation of Saturated Compounds

Distinguish peaks of higher saturated esters at $[M-31]^+$ due to α-cleavage (loss of methoxy group) and $[M-43]^+$ due to the removal of C_{2-4} propyl group was observed at all spectra of waste cooking oil methyl esters (WCOME) mass spectrum. Base peak of saturated WCOME's was observed at m/z = 28, which correspond to the McLafferty rearrangement. As a result of β-cleavage, the first member of cabomethoxy $[CH_3OOC\ (CH_2)\ n]^+$obtained at m/z = 87 where n=2, 3, 4, 5, 6…., m/z 87, 101, 115, 129, 143…, with difference of 14 a.m.u. due to the CH_2 unit, a hydrocarbon series of alkyl ions. McLafferty peak at m/z = 74, β-cleavage and alkyl series support our argument of saturated waste cooking oil methyl esters (WCOMEs). A representative mass spectrum of Tetradecanoic acid methyl ester (C20:0) with mass fragmentation ions is shown in Figure 3. 25.

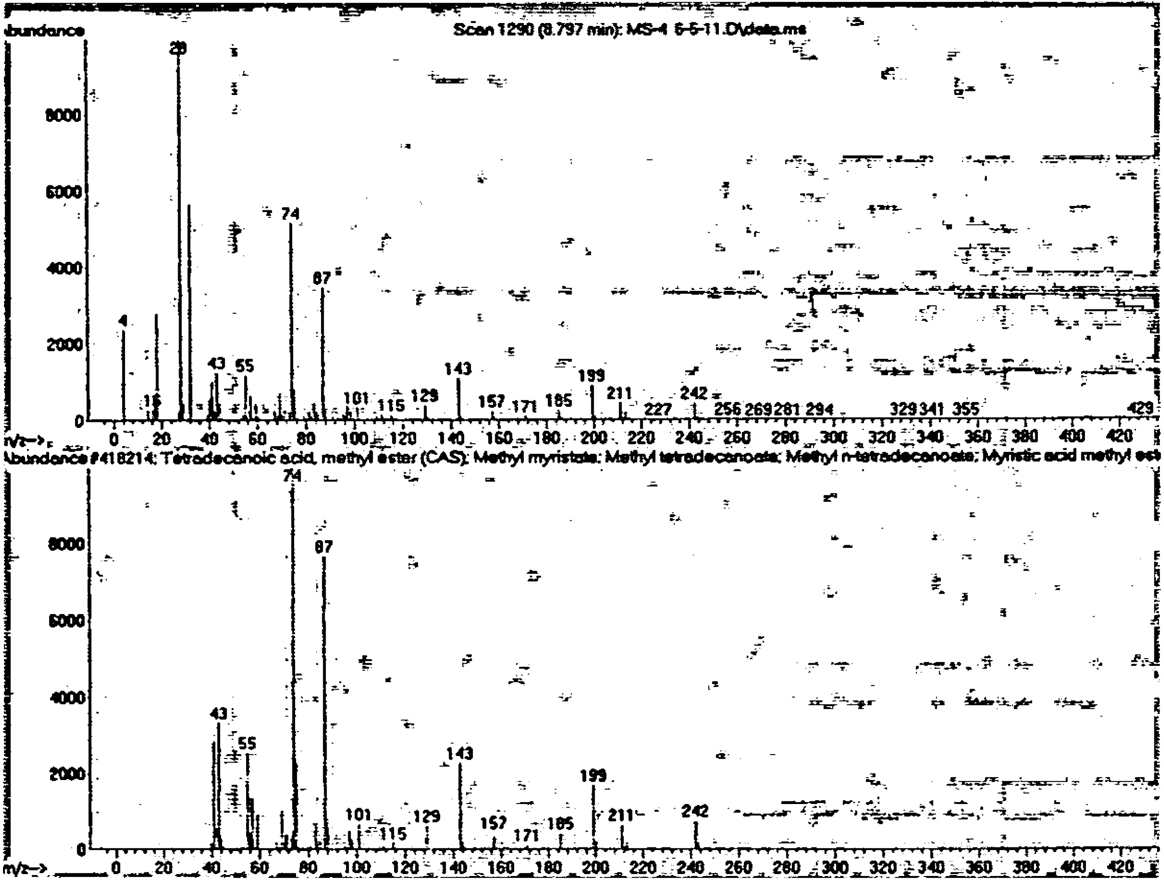

Figure 3.25: MS spectra for Saturated Compound

Investigation of Saturated Compounds

Distinguish peaks at $[M-32]^+$due to loss of methanol and $[M-74]^+$ due to loss of McLafferty ion and base peak at m/z = 55 are the characteristic and distinguishable fragmentation peaks of three major monosaturated esters present in WCOMEs. The characteristic peaks $[CnH2n-1]^+$, $[CnH2n]^+$ appears due to the cleavage at the unsaturation and then the successive loss of 14 a.m.u. (CH_2 unit) leads to the appearance of base peak at m/z = 55 for monosaturated esters in waste cooking oil methyl esters. A representative mass spectrum of 9-Octadecenoic acid methyl ester (C22:1) with mass fragmentation ions is shown in Figure3.25.

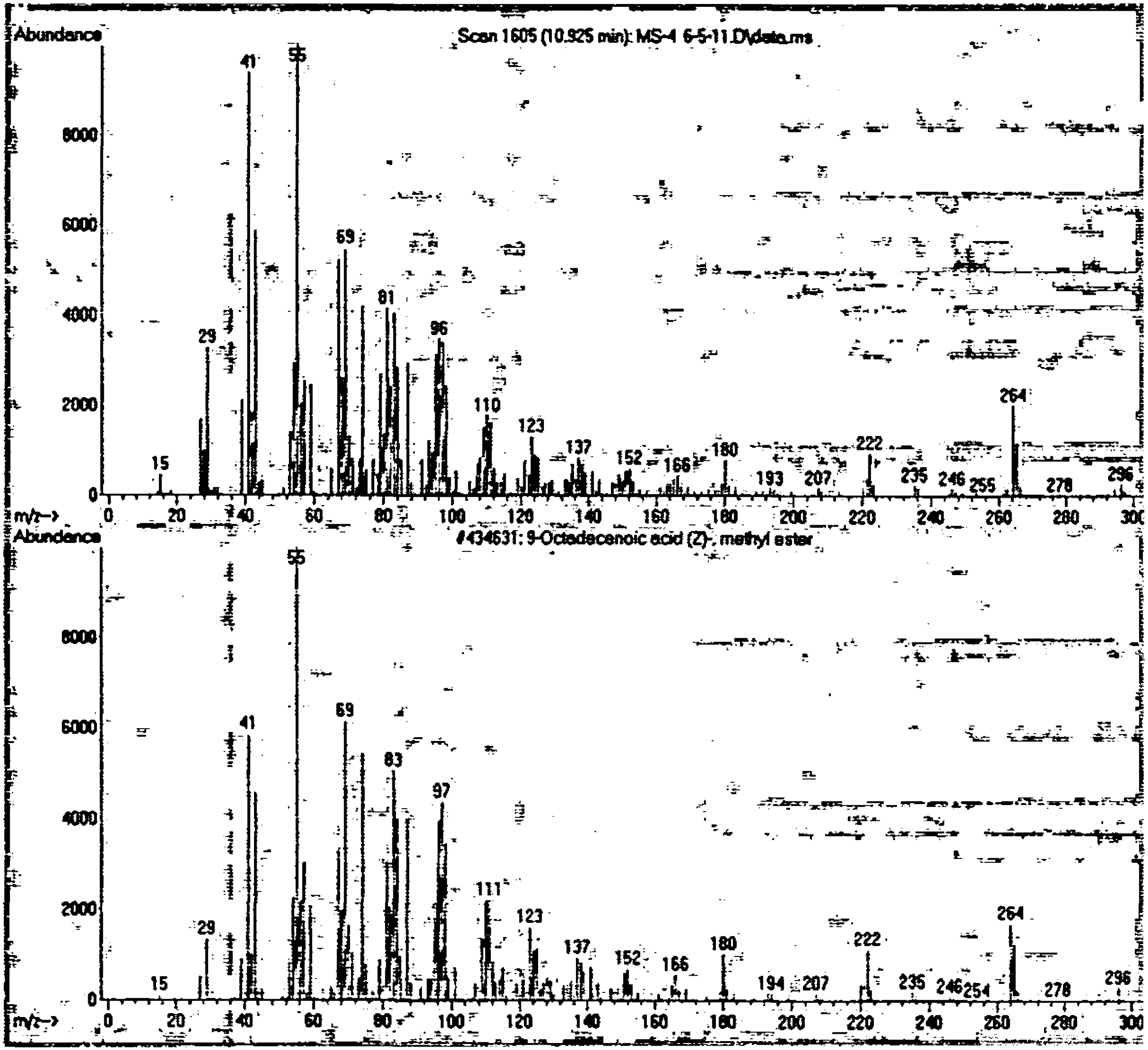

Figure 3.26: MS spectra of mono-saturated compounds

Investigation of Unsaturated Compounds

10, 13- Octadecadienoic acid methyl ester, are the three diunsaturated methyl esters observed in the GC of the waste cooking oil biodiesel. 10, 13-octadecadienoate methyl ester (C18:2) fragmentation showed a characteristic base peak at m/z 41, $[M-31]^+$ due to loss of methoxy group and McLafferty rearrangement peak at m/z =74. Hydrocarbon ions $[CnH2n - 3]^+$ were seen in the lower mass range at m/z 67, 81, 95, 109, 123,137 etc. A representative mass spectrum of 10, 13-Octadecadienoic acid methyl ester (C18:2) with mass fragmentation ions is shown in Figure 3.26.

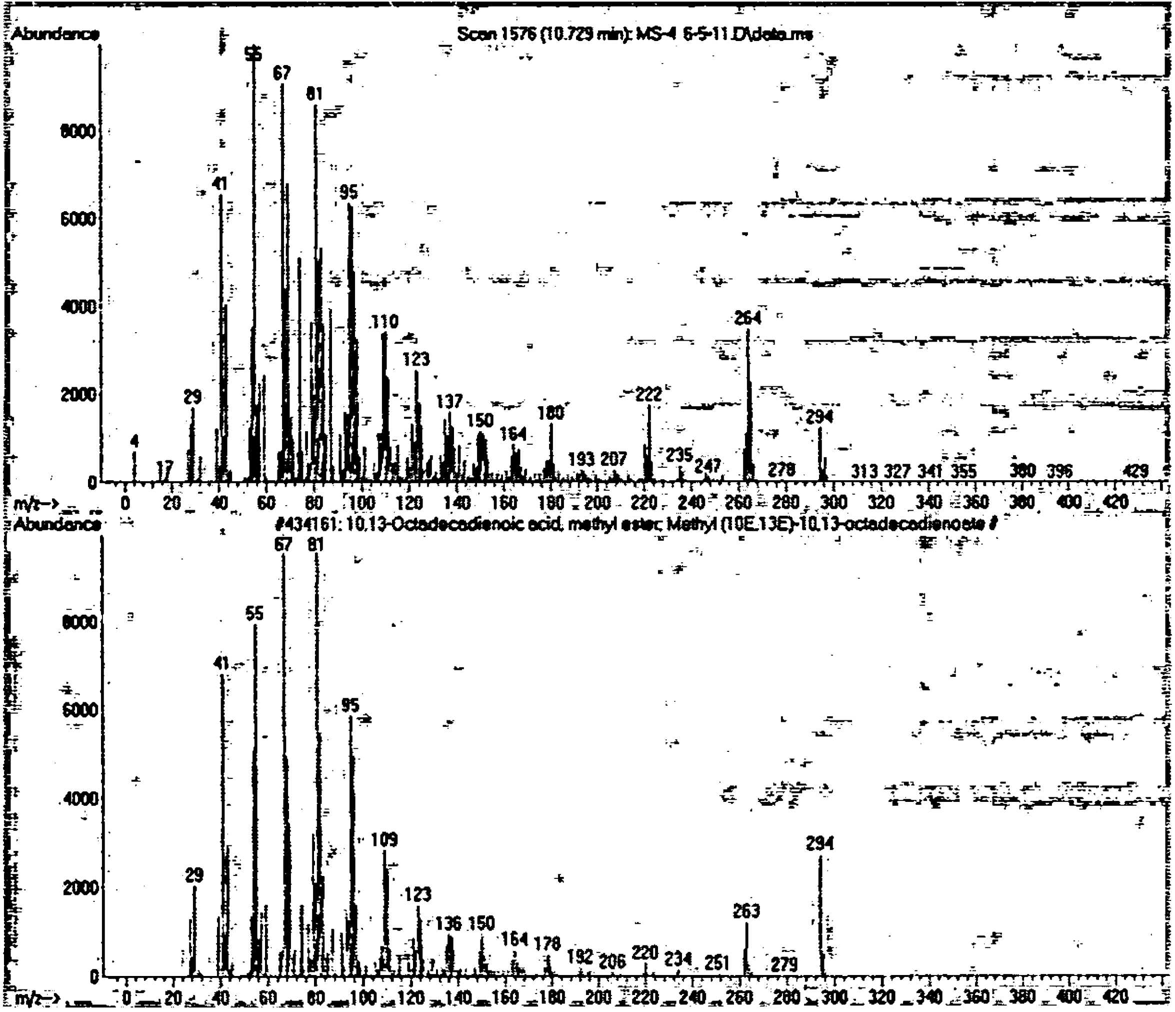

Figure 3.27: MS spectra of Unsaturated Compounds

Identification of Cu_2O-NiO Nano Catalyzed Biodiesel

Table 3.11: Retention Time for MS spectra of biodiesel

Sr. No	Fatty Acid corresponding Esters	Formula	Retention Time (min)
1.	Tetradecanoic acid. methyl ester	$CH_3(CH_2)_{13}COOCH_3$	9.790
2.	9- Hexadedecanoic acid, methyl ester	$CH_3(CH_2)_5CH=CH(CH_2)_2COOCH_3$	10.763
3.	Hexadecanoic acid, methyl ester	$CH_3(CH_2)_{14}COOCH_3$	10.878
4.	10, 13-Octadecadienoic acid, methyl ester	$CH_3(CH_2)_3CH=CHCH_2CH=CH(CH_2)_8COOH$	10.716
5.	9-Octadecenoic acid, methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	11.973
6.	11-Eicosenoic acid, methyl ester	$CH_2(CH_2)_7CH=CH(CH_2)_9COOCH_3$	12.635
7.	Eicosenoic acid, methyl ester	$CH_3(CH_2)_{18}COOCH_3$	12.716
8.	13- Docosanoic acid, methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOCH_3$	13.445
9.	Docosanoic acid, methyl ester	$CH_3(CH_2)_{20}COOCH_3$	13.527
10.	15- Tetracosenoic acid, methyl esters	$CH_3(CH_2)_7CH=CH(CH_2)_{13}COOCH_3$	14.310

Investigation of Saturated Compounds

Distinguish peaks of higher saturated esters at $[M-31]^+$ due to α-cleavage (loss of methoxy group) and $[M-43]^+$ due to the removal of C_{2-4} propyl group was observed at all spectra of waste cooking oil methyl esters (WCOME) mass spectrum. Base peak of saturated WCOME's was observed at $m/z = 74$, which correspond to the McLafferty rearrangement. As a result of β-cleavage, the first member of cabomethoxy $[CH_3OOC\ (CH_2)\ n]^+$obtained at $m/z = 87$ where n=2, 3, 4, 5, 6…., m/z 87, 101, 115, 129, 143…, with difference of 14 a.m.u. due to the CH_2 unit, a hydrocarbon series of alkyl ions. McLafferty peak at $m/z = 74$, β-cleavage and alkyl series support our argument of saturated waste cooking oil methyl esters (WCOMEs). A representative mass spectrum of Tetradecanoic acid methyl ester (C20:0) with mass fragmentation ions is shown in Figure 3.27.

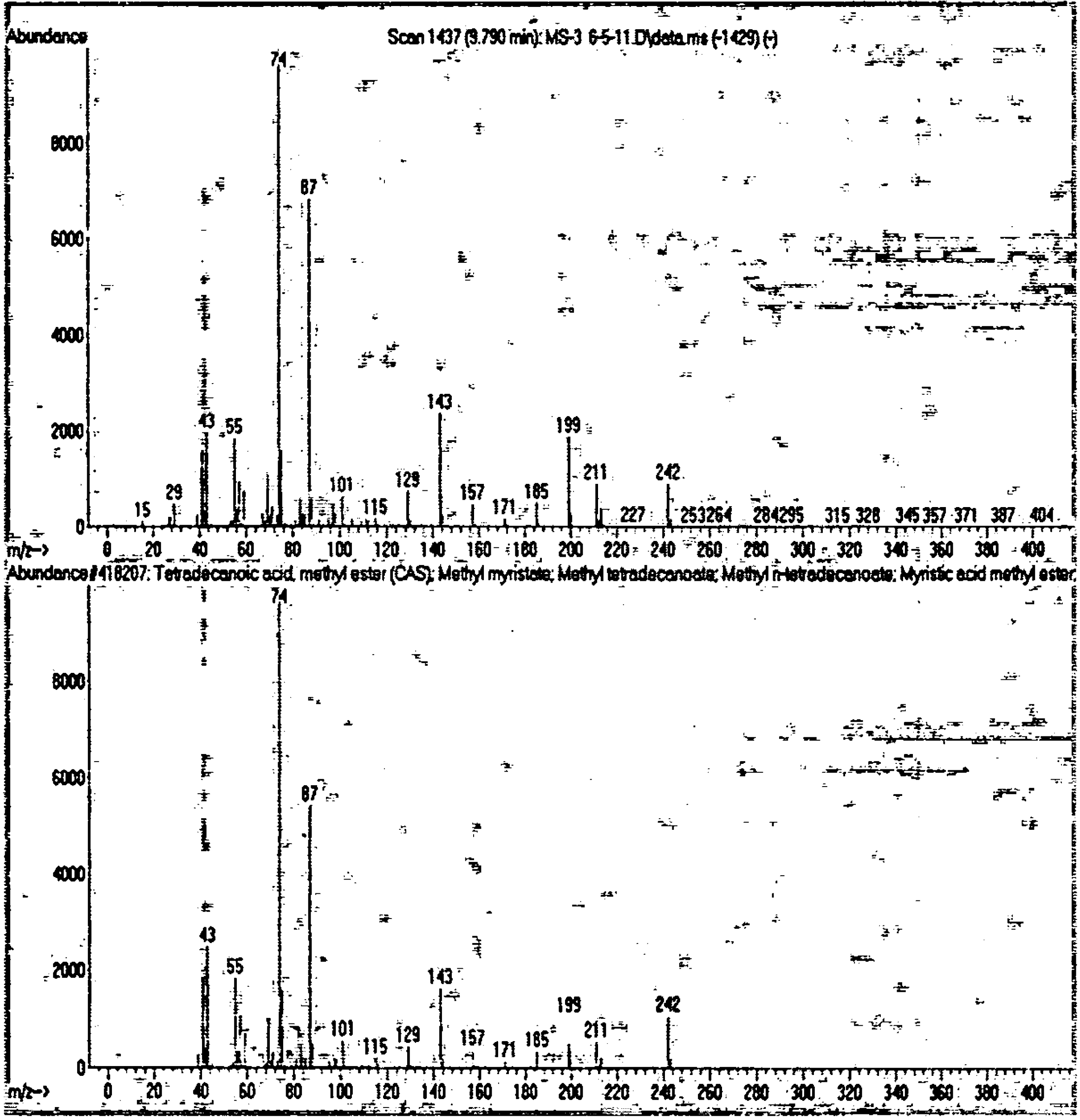

Figure 3.28: MS spectra of saturated compounds

Investigation of Mono-Saturated Compounds

$[M-32]^+$due to loss of methanol and $[M-74]^+$ due to loss of McLafferty ion and base peak at m/z = 55 are the characteristic and distinguishable fragmentation peaks of three major monosaturated esters present in WCOMEs. The characteristic peaks $[CnH2n-1]^+$, $[CnH2n]^+$ appears due to the cleavage at the unsaturation and then the successive loss of 14 a.m.u. (CH_2 unit) leads to the appearance of base peak at m/z = 55 for monosaturated esters in waste cooking oil methyl esters. A representative mass spectrum of 11- Eicosenoic acid methyl ester (C22:1) with mass fragmentation ions is shown in Figure3.28.

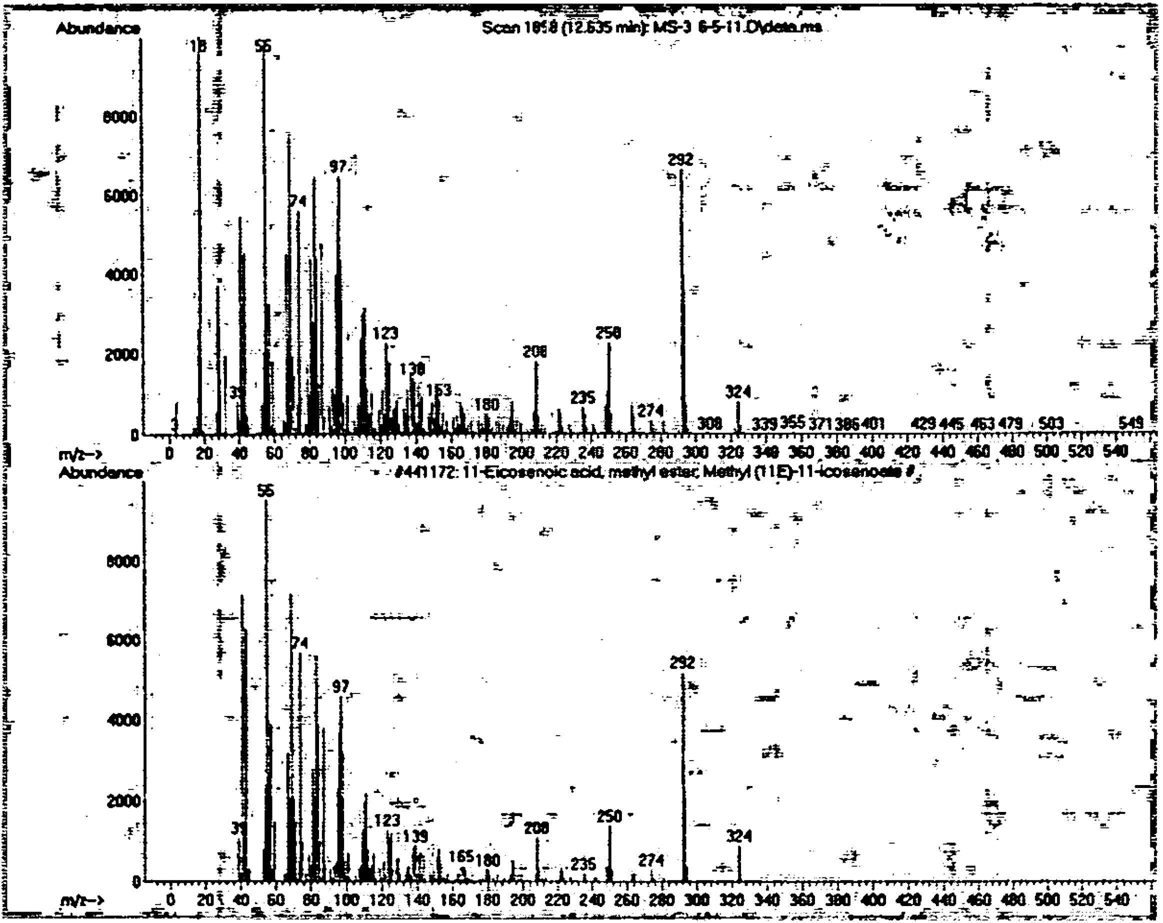

Figure 3.29: MS spectra of mono-saturated compounds

Investigation of Di-Saturated Compounds

10, 13- Octadecadienoic acid methyl ester, are the three diunsaturated methyl esters observed in the GC of the waste cooking oil biodiesel. 10, 13-octadecadienoate methyl ester (C18:2) fragmentation showed a characteristic base peak at m/z 41, $[M-31]^+$ due to loss of methoxy group and McLafferty rearrangement peak at m/z =55. Hydrocarbon ions $[CnH2n - 3]^+$ were seen in the lower mass range at m/z 67, 81, 95, 109, 123,137 etc. A representative mass spectrum of 10, 13-Octadecadienoic acid methyl ester (C18:2) with mass fragmentation ions is shown in Figure 3.30.

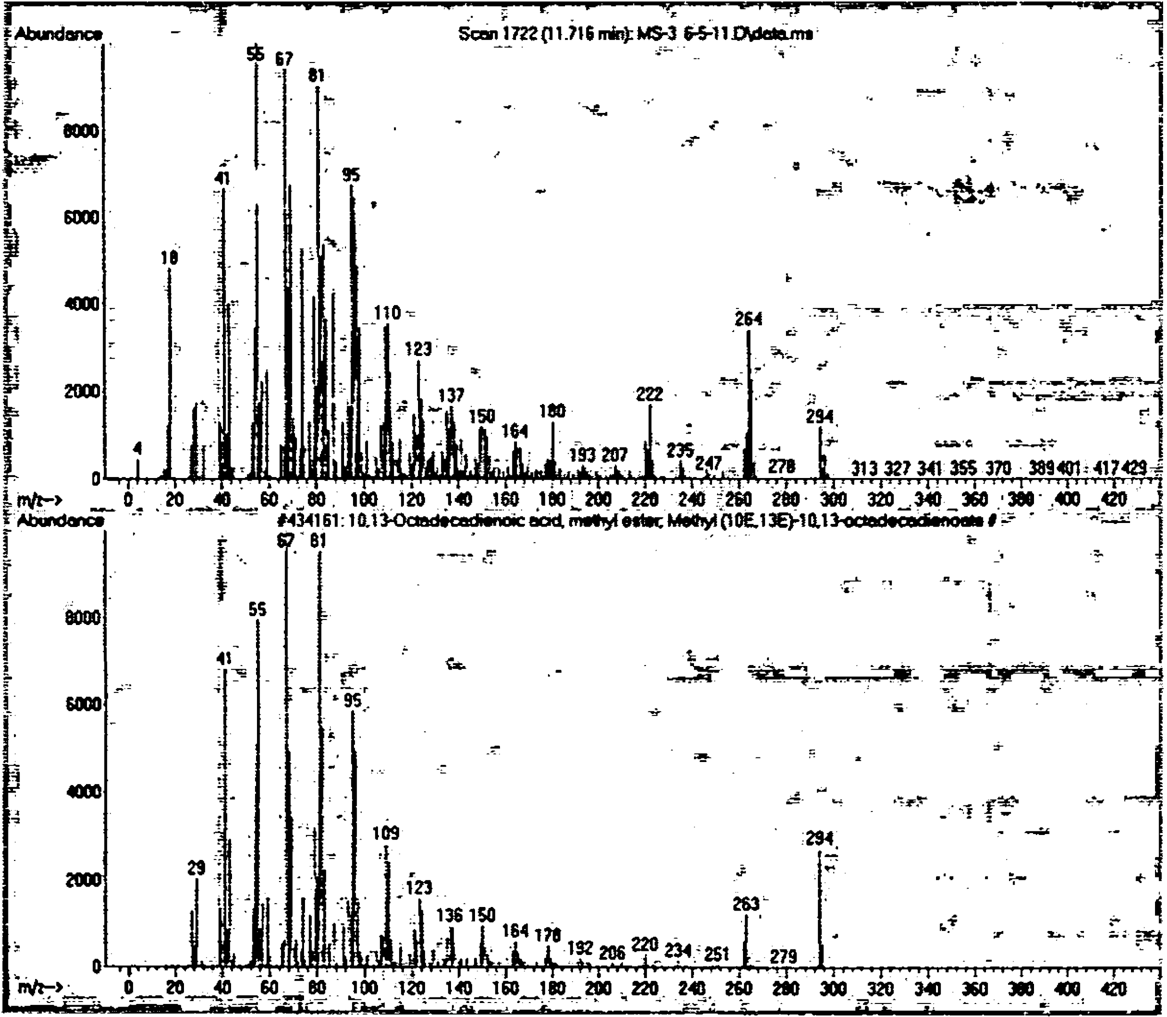

Figure 3.30: MS spectra of di-saturated compounds

CHAPTER #4

CONCLUSION

4 Conclusion

Table 4.1: The Detailed Comparison for Trans-esterification Process between Traditional NaOH Technology, Indigenous NaOH Technology & Nanotechnology

Sr. No.	Attributes (Trans-esterification)	Traditional NaOH Technology	Indigenous NaOH Technology	Nanotechnology
1	**Reaction Time**	**90min**	**26min**	**17min**
2	Reaction Temperature	60-63°C	59°C	40-45°C
3	**Stirring Speed**	**800-1000rpm**	**450rpm**	**150rpm**
4	Settling Time	180min	25min	No settling required
5	**By products (glycerol)**	**50%pure**	**70%pure**	**No by product obtained**
6	De-Sponification Time	150min	30min	No Sponification time required
7	**Total Completion Time**	**480min**	**80min**	**30min**
8	Biodiesel Yield (%)	78-82%	87%	96%

Biodiesel production is worthy of continued study and optimization of production procedures due to its environmentally beneficial attributes and its renewable nature. Nano catalyst synthesized in this study for transesterification is considered to be a green process requiring neither catalyst recovery nor aqueous treatment steps and very high yields of methyl esters can be obtained, close to the theoretical values as compared to the convention method for synthesis by alkali catalysts that produce many raw products.

Nano catalysts proved to be an energy and time efficient method as its reaction completed in less than half an hour acquiring temperature range of 40-45 °C without producing any by-products.

Several conventional methods of transesterification reactions were carried out for studying various aspects including effect of temperature, stirring speed and vegetable oil/ molar ratio of sodium hydroxide. Reaction was completed in 30-40 min depending on the conditions applied. The stoichiometry reaction required 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol was used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Settling time was 2-3 hrs and washed many times for the separation of soap and glycerol .Several aspects have an influence on the course of the transesterification. The best conditions for biodiesel were 30ml methanol ratio in 100 ml of oil having 1% of NaOH used at 60 degree centigrade. NMR studies also confirmed nano catalysts to be more economical as produces 96 % yield and alkali catalyst produced 87 % yield.

Thus alkali catalysts besides adding a layer of cost to biodiesel production, adding water shortens the lifetime of the biodiesel. Secondly alkali catalysts is not suitable for waste cooking oil feedstock used because it contains larger quantities of FFA that instead of producing high yield of biodiesel convert most of the product into soap. So, it is only useful for soya bean type of oil having lower quantities of FFA. When going to cheaper feedstock, nano catalysts synthesized in this study were cheap as well as economical. So, our in-house methods proved to be more economical biodiesel production process, a recyclable catalyst, and a cleaner biodiesel without glycerol. Cost of the biodiesel is reduced to about 10 % than alkali catalyst. Thus "Nano technology is a really attractive technology that we're bringing to the table at the right time"

CHAPTER #5

RECOMMENDATIONS

5 Recommendations:

- Biofuel policies should focus on market development. An enabling environment for
- renewable fuels industry development must be created in order to draw in entrepreneurial creativity, private capital and technical capacity.
- Policies are needed to expedite the transition to the next generation of feedstock and technologies that will enable dramatically increased production at lower costs, combine with the real potential for significant reductions in environmental impact.
- The geographical disparity in the production potential and demand for biofuels will necessitate the reduction in barrier to biofuel trade. Freer movement of biofuels around the world should be coupled with social and environment standards and a credible system to certify compliance.
- To achieve a rapid scale-up in biofuels production that can be sustained over the long term, government must enact a coordinated set of policies that are consistent, long term and informed by broad stakeholder participation.
- In order to achieve their full potential to provide security, environmental and social benefits, biofuels need to represent an increasing share of total transport fuel relative to oil. In combination with improved vehicle efficiency, smart growth and other new fuel sources, such as biogas, eventually, even renewable hydrogen or electricity, biofuels can drive the world towards a far less vulnerable and less polluting , introducing the new era of research in the globe.

CHAPTER #6

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6 REFERENCES:

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