Major Project -II

SOME STUDIES ON SYNTHESIS AND TRIBOLOGICAL PROPERTIES OF BIOLUBRICANT DERIVED FROM CASTOR OIL

Submitted to **Delhi Technological University**
in partial fulfilment of the requirement for the award of the Degree of

Master of Technology
In
Thermal Engineering
By

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July, 2014

DECLARATION

I, hereby declare that the work embodied in the dissertation entitled "**SOME STUDIES ON SYNTHESIS AND TRIBOLOGICAL PROPERTIES OF BIOLUBRICANT DERIVED FROM CASTOR OIL"** in partial fulfilment for the award of degree of MASTER of TECHNOLOGY in "THERMAL ENGINEERING", is an original piece of work carried out by me under the supervision of Prof. Naveen Kumar, Mechanical Engineering Department, Delhi Technological University. The matter of this work either full or in part have not been submitted to any other institution or University for the award of any other Diploma or Degree or any other purpose what so ever.

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CERTIFICATE

This is to certify that the work embodied in the dissertation entitled **"SOME STUDIES ON SYNTHESIS AND TRIBOLOGICAL PROPERTIES OF BIOLUBRICANT DERIVED FROM CASTOR OIL"** by **VARUN PATHAK, (**Roll No.- **2K12/THR/21)** in partial fulfilment of requirements for the award of **Degree of MASTER OF TECHNOLOGY in THERMAL ENGINEERING**, is an authentic record of student's own work carried by him under my supervision.

This is also certified that this work has not been submitted to any other Institute or University for the award of any other diploma or degree.

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ACKNOWLEDGEMENT

It is a pleasure to acknowledge our gratitude to all the people involved, directly or indirectly in the completion of this project. I would like to thank our project guide **Dr. Naveen Kumar** who devoted valuable hours for this assignment and providing the motivational guidance during the entire preparation of this project, answering the number of technical queries despite his busy schedule. His valuable suggestions, constructive criticism and timely help proved extremely fruitful.

I am thankful to Sh. Kamal Nain, Sh. Manoj Kumar and other project staff of Centre for Advanced Studies and Research in Automotive Engineering for all assistance during execution of this project work. I am also thankful to my fellow friends and colleagues who were always there to lend a helping hand in the hour of need.

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ABSTRACT

The world today is facing severe oil crisis and environmental pollution, thus there is a great urgency of developing and applying bio based products as a substitute to mineral oil based products. Rapid industrialization and automation in the last decade has increased the demand of mineral oil based lubricant that will get exhausted in the years to come. Also in addition to the above fact, the biodegradability of mineral-oil based lubricants is around 25% maximum. About 50% of all lubricants sold worldwide end up in the Environment. Due to extensive use of mineral oil based lubricants, several environmental issues such as surface water and groundwater contamination, Air pollution, soil contamination, agricultural product and food contamination are emerging very rapidly.

Due to above mentioned reasons and an increased awareness of people about the adverse effects of mineral lubricants on the environment and an ever increasing demand for cleaner and healthier environment has led the government to make very high order strict regulations for mineral lubricants. Due to this, there is an amplified demand for environment friendly lubricants more over in areas where there are chances of interaction between lubricants and water, food or people. Thus, over the past few years vegetable oil lubricants has come out as a potential substitute to the lubricants derived from mineral oils and they are currently being exhaustively researched by scientists

Lubricants derived from vegetable oils are extremely eye-catching auxiliary to the lubricants derived from mineral oil as these are completely environment friendly, renewable in nature, not-hazardous and fully naturally degradable.

Lubricants derived from vegetable oils are chosen not only because of renewable nature but also because of the fact that they possess great lubricating characteristics like high VI, higher flash-point, lower volatility, great contact lubricating capacity and good solvency with other liquid additives.

However, a high degree of multiple C–C unsaturations in the fatty acid (FA) chain of vegetable oils causes poor thermal and oxidative stability. This fact confines their use as lubricants to a modest range of temperature. In the current work for formulation of bio-degradable lubricants simple esterification reaction was carried out between raw castor oil (RCO) and methanol to form castor oil methyl ester (COME).Also raw castor oil (RCO) was chemically modified via epoxidation to formulate chemically modified castor oil (CMCO) to increase oxidative stability of castor oil. Apart from this, as part of another formulation castor oil was thermally modified to form thermally modified castor oil (TMCO

Finally all the formulated bio-lubricants were subjected to various tribological tests viz. evaporative loss, viscosity index, iodine value, pour point, oxidation stability and four ball wear test. Results were analyzed and compared with conventional lubricant SAE 20W40.The castor oil based formulations showed promising properties to justify themselves to be an excellent substitute to conventional SAE 20W40 oil.

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NOMENCLATURE

A	ampere
ASTM	American society of testing and materials
AW	anti wear
^{o}C	Degree Celsius
cc	Cubic centimetre
CCS	carbon capture and storage
cSt	Centi Stoke
CO_2	carbon dioxide
CO	castor oil
RCO	raw castor oil
TMCO	thermally modified castor oil
COME	castor oil methyl ester
CMCO	chemically modified castor oil
EU	European Union
EP	extreme pressure
F	Fahrenheit
g	Gram
GDP	gross development product
GC	gas chromatograph
Hrs.	Hours
Hz	Hertz
mm	Millimetre
ml	millilitre

Mt	Million Tonnes
Kt	kilo tonnes
Kg	kilogram
No.	Numbers
NMR	nuclear magnetic resonance
ppm	Parts per million
rpm	Revolutions Per Minute
PAO	Polyalfaolefin
RBOT	rotating bomb oxidation test
RPVOT	rotating pressure vessel oxidation test
ρ	Density
%	Percent
TG	Tri Glycerides
FAME	Fatty Acid Methyl Ester
FAEE	fatty acid ethyl ester
FFA	free fatty acid
FTIR	Fourier transform infrared spectroscopy
VI	viscosity index
V	volts

CHAPTER 1

INTRODUCTION

A lubricant is a substance used to facilitate relative motion of solid bodies by minimising friction and wear between interacting surfaces. Lubricants can be considered as constructional elements or engineering fluids which have to be kept on the newest technological level because of the continuous development of tribological systems.

As a product group, lubricants play an essential role in industry and transportation: without lubrication, there is no transfer of energy. Reduction of friction and wear by use of lubricants enables machinery to work without premature failure, results in energy savings and controls emissions. Related functional fluids are used in applications where their primary purpose is not just friction and wear reduction, although some degree of lubricity may be required. Examples of such applications are hydraulic fluids, electrical transformer fluids, heat transfer fluids and metalworking coolants. Apart from high-volume applications such as engine, gear and hydraulic fluids, there are thousands of other specifically tailored lubricant or grease formulations that differ greatly in composition, both chemically and physically.

Lubricants represent considerable economic and ecological importance. Recently, in this context, saving resources and energy and reducing emissions have become essential matters. Lubricants have a particularly important contribution to make in relation to energy conservation, minimisation Lubricants: properties and characteristics of waste and development of durable products. Correct lubricant selection can lead to improvements in energy efficiency of up to 10%. Minimising wear by efficient lubrication prolongs the useful life of machines, thereby decreasing the consumption of non-renewable resources.

Industrial production processes can reach higher levels of efficiency and products can be made more attractive through the added value offered by lubricants. Truly green lubricants are those that optimise energy efficiency and minimise wear in the machinery they lubricate and have maximised service lifetimes in order to reduce the amount of lubricant required [1].

Adoption of high performance lubricant technologies has led to a significantly lower lubricant consumption. Modern high-performing commercial lubricants are usually complex materials composed of a lubricant base stock formulated with an additive package for specific property enhancement of the resulting full lubricant formulation.

1.0 PURPOSE OF LUBRICATION

Tribology (Greek tribos, or rubbing) is the science and technology of interacting surfaces in relative motion and brings together all major disciplines involving friction, wear and lubrication. The term was originally coined by Jost in 1966 [2] who drew attention to its interdisciplinary nature and the large savings that proper application of tribology could produce. The aim of ‘green tribology’ is to save energy and materials and to enhance the quality of life and the environment.

A tribological system consists of four elements: the contacting partners, an interface with an enclosed medium (lubricant), and the environment. Tribo systems are present in all mobile mechanisms, from automotive, industrial and domestic to aerospace applications. In tribo systems, one material slides against another or against itself. For each combination of materials and contact configurations, the tribological variables include the type of movement, normal applied load, sliding distance, speed and frequency, duration of the applied stress, temperature (ambient and contact temperature), atmosphere, moisture, lubricating mode, etc. Tribometric parameters are friction, wear and temperature. Specific devices, called tribometers, are used to measure friction and wear.

Tribology is a fast-growing discipline generating much interest in academia, industry and other research centres. Because of its highly interdisciplinary nature, tribology requires efficient cooperation between mechanical engineers, materials scientists, metallurgists, chemists and chemical engineers, physicists, surface scientists, with contributions of specialists in environmental protection and toxicology.

The primary objective of lubrication is to reduce friction, wear and heat between contacting surfaces in relative motion. While wear and heat cannot be eliminated completely, both effects can be reduced to acceptable or even negligible levels. They can be minimised by introducing a material (the so called lubricant) with low shear strength or coefficient of friction between the wearing surfaces.

Lubricants are used to control friction and wear preventing direct contact between the surface asperities of the materials and lowering the contact temperature. Lubrication is meant to prevent scuffing, together with scoring, seizure and similar severe damage of friction surfaces [3]. Scuffing induces the heaviest damage in friction pairs, usually producing failure of the tribosystem. The lubricant must protect the component that it lubricates. In some cases, this protection is in the form of a fluid film that keeps opposing surfaces separated. In other cases, the lubricant provides wear protection by forming a chemical film on a surface.

The lubricant transports protective chemicals to the sites where they are needed and transports waste products away from the sites where they are generated. Scuffing is caused by the breakdown of lubricant films on the rubbing surfaces. The rupture of films is due to mechanical and/or thermal loads, which in turn depend on the parameters of the tribosystem, such as sliding and rolling speeds, temperature and friction state. The geometry of the contact and the contact pressure change when one or both materials are worn during the sliding process. When wear debris is trapped at the contact zone, a third body is formed which can increase the surface damage by abrasion.

Tribosystems require adequate material selection, wear protection by special coatings and surface engineering, lubrication and lubricants, modern test equipment in laboratories and test fields. Scientific focus on lubrication technology and lubricants is relatively new. Lubrication is critical for wear protection of mechanical systems that should operate for extended periods of time.

The various benefits of using lubricants can be summarized in the points below as:

- Reduction of friction
- Wear and corrosion protection

- Shock cushioning
- Heat transfer
- Seal action
- Insulation
- Production efficiency
- Component lifetime (equipment durability)
- Energy economy

Lubrication may also be used for other purposes, namely to:

- reduce oxidation and prevent rust;
- reduce energy consumption;
- provide insulation in transformer applications;
- transmit mechanical power in hydraulic fluid power applications; or
- Seal against dust, dirt, and water (flushing out contaminants).

A major goal of current tribological research is to find effective lubricants for reactive light alloys such as magnesium, aluminium and titanium, which are of interest in the automotive industry in view of their lower densities and the ability to form corrosion-protective surface layers.

Commercial lubricants are mainly derived from petroleum, present environmental problems and are not suitable for many materials and conditions. Consequently, the need for new, effective, environmentally friendly lubricants is clear, especially as losses due to friction and wear caused by poor lubrication are estimated at about 1.5% of the gross domestic product (GDP) of industrialised countries [5].

1.1 FORMULATION OF LUBRICATING OIL

All lubricant systems are materials formulated from one or more base fluids (native oils, synthetic esters, etc.) and property-enhancing chemical substances, commonly called additives. The percentage of additives in a formulation differs greatly, from hundreds of ppm level for antifoam agents and biocides to 1% in simple compressor oils and up to 30% in metalworking fluids and gear lubricants. On average, lubricating oils consist of 93% base oil(s) and 7% additives [6]

A base fluid means a lubricating fluid whose flow, ageing, lubricity and anti-wear (AW) properties, as well as its properties regarding contaminant suspension, have not been altered by the inclusion of additives.

1.1.0 Lubricant base stocks

Fatty acid-based products from vegetable and animal origins used to be the main source of lubricants up to and beyond the late 19th century when mineral oils began to become available in large volumes at increasingly competitive prices. For a time, blends of mineral oil and natural fatty acid products, referred to as fatty oils, and were widely used. Since the 1950s and until recently the trend has been towards lubricants and functional fluids with solely petrochemical bases and containing additives from petrochemical or synthetic sources. With the overwhelming quantity of mineral lubricant base oils, lubricants are generally viewed as an integral part of the petroleum industry.

Now industry and end-users are gradually turning again to more environmentally friendly products. Some recent high-performance lubricants no longer contain petroleum base oils. Increasing demands on lubricant performance and eco-compatibility have led to the development of more pure oils, such as hydrocracked products, poly-α-olefins and esters. Approximately 7–10% of base oils are now synthetic products (including hydrocracked oils). Also natural fatty oils are experiencing a come-back as their oleo chemical derivatives because of rapid biodegradability. Lubricants are broadly distinguishable on the basis of their origin: mineral, synthetic and fixed oils.

1.1.1 Mineral oils

More than 90% of the lubricant market is dominated by mineral and related oils, which are heavily contaminating the environment but have a wide availability and low price. Development of lubricating oils (from crude oil to base stocks and full formulations) is a sophisticated technology. The process of converting crude oil into finished mineral base oil is called refining (by distillation, de-asphalting, acid refining, solvent extraction, solvent dewaxing, etc.). Base oils obtained by processing of crude petroleum are classified as refined and residual compounded. Bright stocks are highly viscous base oils (viscosity > 45 cSt at 100 °C).

Most lubricants used today, in thousands of different technical applications, are traditionally still mineral oil-based. Advances in lubricant technology have brought green products to the forefront in many high-profile applications in environmentally sensitive areas as mineral oil based lubricants are highly toxic in nature and non-biodegradable in nature. Also it is from the fact that the mineral oil based lubricants are petroleum based products which are fast depleting due to rapid utilization in the last few decades.so the mineral oil based lubricants today are facing dual problem of environmental pollution and availability of oil. This has led the researchers to shift their focus on new and greener technologies as in bio lubricants. Over time, the ongoing development of next-generation lubricants has gradually shifted focus from biodegradable to renewable (bio-based) and to sustainable, with emphasis on energy economy.

1.2 OIL CRISIS

The growth of human being has travelled a long journey. It was the greatest achievement of primitive man when he discovered fire with the help of a stone. With this human history moved very fast. Later on a number discoveries and inventions were made which changed human life completely

Abundant and economical oil is the life blood of modern civilizations. Adequate availability of inexpensive oil is the most important demand of today. Economic growth and industrialization both are dependent on the availability of oil. Many of the developed Western-European countries as well as developing countries such as India depends to a great extent on imports of oil resources to meet the bulk of their requirements. But today the world is facing twin crises of fast depleting world oil sources on one hand and environmental degradation on the other. This has put the world in a grip of oil crisis. [7-9].

In the case of the developing countries, the oil sector assumes a critical importance in view of the ever-increasing oil needs requiring huge investments to meet them. The Internal combustion engines have revolutionized the world in last hundred years but also contributed significantly towards environmental degradation and an exponentially rapid utilization of oil resources.

There is shortage of oil resources in the world. This problem is related to the insufficient oil resources leading to the shortage in supply which in turn is not able to meet growing demands of oil in the rapidly expanding industrial, transport, agricultural and urban sectors. The condition of India is no better, with growing population and industrialization the demand for oil is increasing day by day.

Petroleum oil and lubricating Oil cover most of the world oil needs and notwithstanding the many and varied projections as to probable time scales, it must be conceded that present sources of such non-renewable resources are finite and that whatever quantities remain must become increasingly more difficult (costly) to win.

Nevertheless, fossil fuels are not considered sustainable and are also questionable from an economic, ecological and environmental point of view. It should also be realized that, as the more accessible deposits become depleted, the global distribution of those remaining will attract progressively heightened political attention, since not all nations can assume proportional future supplies. The recent increase in petroleum prices and the growing awareness related to the environmental consequences of the fuel over-dependency have stimulated the recent interest in alternative oil sources [9-10].

In this scenario, non-edible oils and its derivative – bio lubricant provides a sustainable solution to the problem. By replacing a substantial amount of mineral oil as a base stock for lubricant with an alternative plant oil base stock will surely serve for the dual problem of fast depletion of mineral oil and environmental pollution. Alternative oil source are considered very promising to play an important role in meeting the world’s oil requirements [11-12].

1.3 OIL SCENARIO

With the dawn of the Bronze Age about 3,000 years ago, mankind started on the path to industrialization. In the industrially advanced world of today, the demand for oil is increasing exponentially.

World today is naturally anxious to think about future, because knowing the bitter truth that a day will ultimately come when no more oil will be available. It will mean severe oil crisis. Oil is one of the most important factors concerned for socio-economic development of any country. Many developing countries are not able to fulfill their oil demand from the resources available in their own country and have to depend on other countries for accomplishing it.

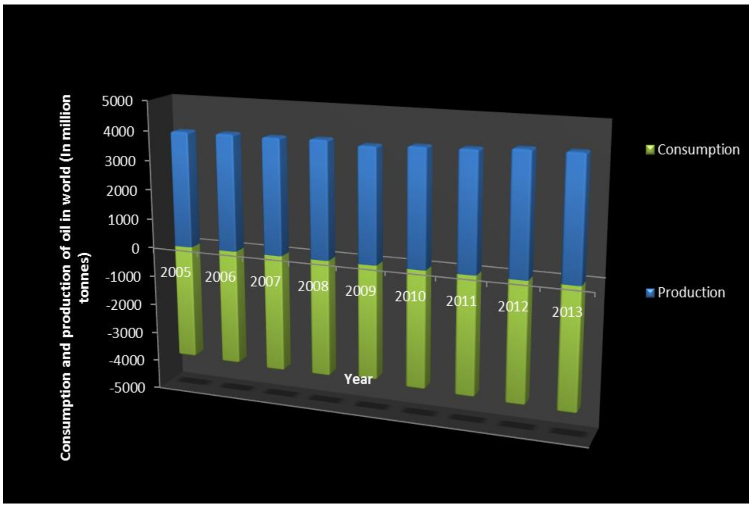


Figure 1.1: world oil production and consumption (million tonnes) [13]

Supply and use to oil economic development at present,' oil poverty' hinders the economic and social development of very large numbers of people. The Indian economy is at a critical stage of development where oil requirement is increasing at a phenomenal pace. Even though, large part of the developed world is struggling to recover from the recession, the relatively faster emerging countries like, China and India are attempting to meet the requisite demand for oil. India has the limited domestic availability of oil, and is compelled to import over 75%-80% of its domestic requirement and subject to the vagaries of a volatile international price scenario.

India is rich in coal and abundantly endowed with renewable energy in the form of solar, wind, hydro and bio-energy, however, its hydrocarbon reserves represent only 0.3% of the global reserves and India is mainly dependent upon crude import to sustain its growth. The exploitation of these resources is very much limited.

India is amongst the fastest growing economy of world and use of oil extensively to sustain its growth. As India does not have huge reserves of petroleum products, it heavily dependent upon the import of petroleum products to cater its need .Despite larger initiatives taken by government; exploration of new sources, rising prices, insufficient supply and limited reserves of petroleum have imposed against burden on country’s forex exchange.

In the year 2013, Indian crude oil production is 42 million tonnes which is 2.4 % higher than during the year 2012 while the consumption of crude oil in 2012 was 173 million tonnes. And in the year 2013 is 175.3 million tonnes [13].

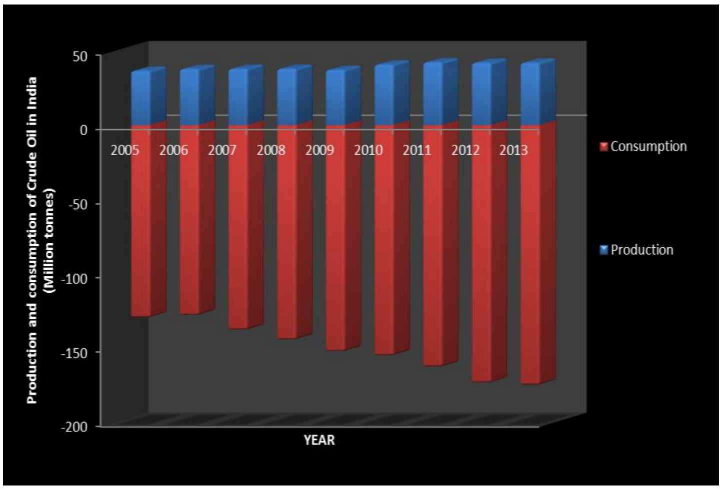


Figure 1.2: India production and consumption (million tonnes) [13]

Thus India being an oil deficit country, it is almost completely dependent on oil imports from other countries. India imported 171.73 million tonnes of oil in the year 2011-2012 which went on to increase to 184.8 million tonnes during the year 2012-2013 [13]

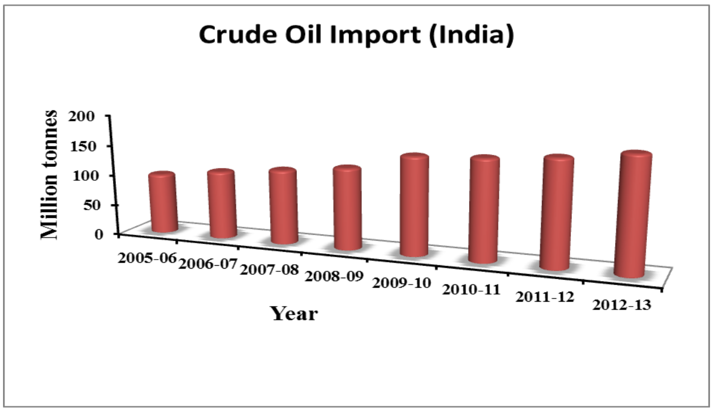


Figure 1.3: India crude oil import (million tonnes) [13]

1.4 ENVIRONMENT DEGRADATION DUE TO MINERAL OIL BASED LUBRICANTS

Numerous fluids used as lubricants are mineral oil based. Because of their low biodegradability and high toxicity, mineral oils are not environmentally friendly. The environment is becoming increasingly contaminated with numerous kinds of pollutants, so any reduction is beneficial. Lubricants are not particularly problematic compared to a number of other chemical products being released into the environment. However, every day, a large portion of lubricants pollute the environment either during or after their use. This lubricant can be technically desirable as in total-loss lubrication and as the result of mishap, such as leaks, emissions, spillages or other problems will affect the environment.

Lubricants and functional fluids are omnipresent due to their widespread use. They pollute the environment in small, widespread amounts and rarely in large, localized quantities. In certain applications, strict specifications on various environmental matters have become mandatory. This has enormous implications for the environment and will endanger climate control. Climate protection is one of the great challenges of the 21st century. In order to reduce CO2 emissions by 2050, there will eventually have to be massive, much disputed and expensive carbon capture and storage (CCS) projects. More efficient processes are better than CCS. Alternative energy sources are becoming increasingly important because the petroleum supply may not always be available. Petroleum crude oils are also expensive and are involved in many political situations.

Concerns about environmental pollution caused by many chemicals, including lubricants, have created a growing worldwide trend of promoting new environmentally friendly products. In Europe, some 1.1 Mt/ yr. of used lubricating oils (representing 20% of total market) are not traceable. It has been estimated that about 600 kt of total-loss lubricants – including chainsaw oils, mould release oils, two-stroke engine oils, chassis and wheel flange greases – are released into the environment every year in the European Union alone [14], for other release estimates, see ref. [15]. Whatever the precise figures, approximately 50% of all lubricants used worldwide end up somehow in the environment via total-loss applications, evaporation, spillage or accidents [16]. Estimates for the loss of hydraulic Fluids are even higher (70–80%) [17-18]. currently, over 95% of these materials are mineral oil-based or synthetic oils. Mineral oils are toxic for mammals, fish and bacteria. Replacing petroleum base oils with biodegradable products is one of the ways to reduce the adverse effects on the ecosystem caused by the use of lubricants. The potential use of renewable raw materials (be it starches from corn, tapioca, wheat or potatoes, cassava or sorghum, chitin, vegetable oils or animal fats, cellulose or algae biomass) in the lubrication industry is currently of great interest [19].

1.5 NEED FOR BIO-LUBRICANTS (RENEWABLE LUBRICANTS)

The ever-increasing global population is faced with various future constraints in growth regarding its very basics of subsistence, such as the availability of fresh water, raw materials, energy and suitable land, abundant and affordable food production, coupled with the need for lower emissions and less waste, and mitigation of the anticipated climate change. This requires truly sustainable technologies and practices. The concept of sustainability dictates that modern technologies should be founded on renewable resources.

The current petroleum-based economy cannot be sustained indefinitely, although naphtha is still likely to remain the main input for the chemical industry for the next few decades, despite the end of cheap conventional oil [20-22]. Prognoses of worldwide petroleum reserves are uncertain and are regularly being scaled up but generally predict maximum production levels around 2020–2030.At increasing oil prices new exploration and drilling technologies are being developed. However, exploitation of shale fields by hydraulic fracturing (fracking) is not without risks (groundwater pollution) and draws significant opposition.

At present, 86% of oil is used for transportation as gasoline, diesel and kerosene (55%), and energy and heating (31%), leaving only 14% to the chemical industry for transformation into a great variety of chemical products. This share might increase somewhat by more efficient engine and heating systems and increasing amounts of biofuels. Deployments of renewable raw materials for the chemical industry and sustainable energy will require a concerted effort from scientists across a great number of disciplines to develop new technologies, and (most of all) political will. Industrial production processes can reach higher levels of efficiency and products can be made more attractive through the added value lubricants can offer.

A lubricant is a substance used to improve the ease of movement between surfaces [23]. Lubricants are used to reduce friction, reduce wear, and prevent overheating and corrosion. They are complex products; usually consisting of 70–99% base oils admixed with additives that modify the natural properties of the fluid to meet its intended requirements. Lubricants represent considerable economic value, enabling high manufacturing speed, avoiding material failures in transportation and industry, and limiting downtime. Their cumulative benefits extend far beyond the tonnes produced.

Today, market demands for lubricants are increased environmental compatibility, reduced emissions, greater occupational safety and, above all, superior performance (including longer lifetime and energy efficiency). The global volume of lubricants used in various industrial applications, especially engine oils and hydraulic fluids, is considerable (about 40 Mt/yr.). Demand for lubricants in the United States is about 2.8 billion gallons (2006), and mainly on account of process oils and high-performance lubricants.

Most of these products (e.g. general industrial oils, engine oils, transmission and hydraulic fluids, gear oils and greases) are as yet still based on mineral oils. Concerns about environmental pollution caused by many chemicals, including lubricants, have created a growing worldwide trend of promoting new environmentally friendly products. In Europe, some 1.1Mt/yr of used lubricating oils (representing 20% of total market) are not traceable. It has been estimated that about 600 kt of total-loss lubricants – including chainsaw oils, mould release oils, two-stroke engine oils, chassis and wheel flange greases – are released into the environment every year in the European Union alone [24]; for other release estimates, see ref. [25]. Whatever the precise figures, approximately 50% of all lubricants used worldwide end up somehow in the environment via total-loss applications, evaporation, spillage or accidents [26]. Estimates for the loss of hydraulic fluids are even higher (70–80%) [27-28].

Currently, over 95% of these materials are mineral oil-based or synthetic oils. Mineral oils are toxic for mammals, fish and bacteria. Replacing petroleum base oils with biodegradable products is one of the ways to reduce the adverse effects on the ecosystem caused by the use of lubricants. The potential use of renewable raw materials (be it starches from corn, tapioca, wheat or potatoes, cassava or sorghum, chitin, vegetable oils or animal fats, cellulose or algae biomass) in the lubrication industry is currently of great interest [29]. Growing concern about the use of mineral oils as lubricants has promoted extensive research into developing and using derivatives of vegetable oils as alternative base oils for environmentally benign lubricants. Interest in the production of biodegradable, environmentally acceptable esters for biodiesel, lubricating base oils, solvents, surfactants, etc., from vegetable oils has increased greatly in recent years. Utilisation of natural materials and green processes in the lubricant industry is especially attractive [30].

Bio lubricants can typically be made from plant oils such as rapeseed, soybean, sunflower, palm and coconut, wax esters and plant polymeric carbohydrates. Since the cost of a lubricant is considerably higher than that of an equal volume of fuel, the use of oleo chemicals as raw materials for lubricants makes good economic sense. Replacement of petroleum by more widely distributed renewable raw materials in an agricultural product-based economy is an enormous challenge and requires integration of the biological and chemical sciences with development of the chemistry, modification, blending, processing, manufacturing and testing of agricultural products. Brazil is a good example of valorisation of biomass. Non-food biomass is the only practical sustainable source of carbon in the long run [31-32]. Bio lubricants are usually considered to be lubricants that have high biodegradability and low human and environmental toxicity [23, 33].

Bio lubricants that meet specific biodegradability and toxicity criteria can be based both on renewable, agricultural raw materials and on petroleum oils or synthetic esters [33-34]

Criteria of consumer acceptance adopted in various countries are different. Some countries only require 50% of the oil to be renewable; others impose utilisation of bio lubricants when near non-navigable waters. Bio-based lubricants are part of an overall green chemistry solution for obtaining better, environmentally safer and more economical lubrication, and for creating efficiencies in manufacturing plants, end products, or in house fleets and maintenance programmes.

Development of bio-based high-performance lubricants requires insight in the relationship between physicochemical and tribological properties of the bio-based ingredients. While biodegradability nowadays is one of the most important design parameters for base oils and lubricant formulations Therefore, an adequate balance of properties is needed. Another important objective of the lubricant industry is formulation of new environmentally friendly lubricants of high technical reliability with similar or better technical specifications than those based on mineral oils, in particular both improved kinematic viscosity values and adequate viscosity thermal susceptibility [35-36].

Bio-based materials have clear advantages and are already economically competitive in a growing number of industrial sectors but further development work is required to achieve additional cost reduction. Plant oils are also attractive alternatives as raw materials for the chemical industry. Bio-lubricants are now available for numerous applications, with performance in competition with that of mineral oil-based products (ranging from worse to comparable and sometimes even better). Lubricant base fluids based on renewable raw materials have been reviewed in the past [26, 37-49]. Consumer acceptance of renewable lubricants depends largely on how well they perform during high-temperature oxidation and low-temperature applications. A wide variety of (chemically modified) vegetable oils has been evaluated in terms of their thermal, oxidation and low-temperature behaviour for their potential use as base fluids for industrial and automotive lubrication.

1.6 BIOLUBRICANTS

Lubricants make up for a large market world over. The usage of lube oils is being estimated to be 37 million metric tonnes in a year for various purposes [50].Lubricants are highly used for industrial and automotive divisions for lubricating machines and all movable bodies. Automobile lubes stands as the largest cluster of lubricants used world over followed by hydraulic lubes. Almost all lubricants of new age are dense formulations having 80–90 percent oils that are used as base are blended with additives to change their inherent characteristics like cold temperature stabilization, oxidative stability, viscosity and VI to be used in a specific application.

A large number of base oils are nowadays accessible from market for formulating lubricant such as mineral base oils, synthetic origination base oils, refined vegetable oils etc. Among all the existing choices, lubricants that are being derived from mineral oil as base oils are the ones that are very commonly used. Though, they are not naturally degradable and chemically hazardous in nature [51].

The natural degradation of mineral-oil based lubricants is only up to 25 percent. It is a known fact that 50 percent of all lubricants used worldwide for various purposes are disposed of into the Environment through complete loss applications, spilling, volatile nature of application and accidents being the major reasons for the loss [52]. Loss of hydraulic lubes is the highest that is about 75-85 percent. The amount of waste oil getting drained into ground or into sewers or ending up in rivers is way too higher than being neglected [53].

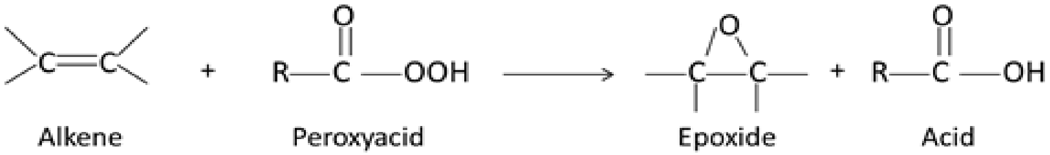
Large order utilisation of lubricants that are being derived from mineral oils are one of the foremost reasons for number of environment issues like surface water pollution and groundwater pollution, Air pollution, soil pollution and food contamination [54].

Due to above mentioned reasons and an increased awareness of people about the adverse effects of mineral lubricants on the environment and an ever increasing demand for cleaner and healthier environment has led the government to make very high order strict regulations for mineral lubricants. Due to this, there is an amplified demand for environment friendly lubricants more over in areas where there are chances of interaction between lubricants and water, food or people. Thus, in the past few years vegetable oil lubricants has come out as a potential substitute to the lubricants derived from mineral oils and they are currently being exhaustively researched by scientists [55].

Lubricants derived from vegetable oils are extremely eye-catching auxiliary to the lubricants derived from mineral oil as these are completely environment friendly, renewable in nature, not-hazardous and fully naturally degradable. Lubricants derived from vegetable oils are chosen not only because of renewable nature but also because of the fact that they possess great lubricating characteristics like high VI, higher flash-point, lower volatility, great contact lubricating capacity and good solvency with other liquid additives [56]. It is a known fact that about forty thousand metric tonne of bio-lubricants are being traded throughout the EU in a year and almost a comparable quantity in the US [57], chiefly for utilisation as a hydraulic lube oil .It has been a very known fact now that a huge quantity of lube oils derived from the mineral oils can be substituted by bio lubricants giving it a probable business of about 5.1 billion US dollars [58].

But, apart from all the good characteristics mentioned above the lubricants derived from vegetable oils have some hitches also like reduced low temperature flow i.e. pour point, very low oxidation stability (mainly caused by the existence of C=C) [59].Nevertheless, reduced low temperature characteristics of lubes derived from vegetable oils can probably be answered by using a wide variety of additives available in the market nowadays [60].The oxidation stability of the lubricants derived from vegetable oils can be enhanced by carefully carrying out selective hydrogenation of C=C unsaturation existing in the structure of fatty acid chain of plant oils [61] or by conversion of C=C unsaturation to oxirane ring by a chemical process known as epoxidation [62-63].A large number of reactions can be done under adequate reaction environments by alteration of C=C unsaturation to oxirane ring [64] and hence, this process without a doubt got added attention in contrast to hydrogenation of C=C unsaturation and hence in the current research also epoxidation was chosen as the use of this reaction showed a significant improvement to being getting oxidised.

Epoxidation reaction is a reaction of C=C bonds present in vegetable based oils with lively oxygen that results in the adding of an oxygen atom in the double bond, changing the original double bond into a three membrane epoxide oxirane ring [65].



One of the methods followed in the industries for epoxidation reaction is situ epoxidation process. In this process, generally we make acetic/formic acid to react using hydrogen peroxide in the existence of sulphuric/phosphoric acid [66]. However, it is seen that if we use very strong mineral acid in the epoxidation reaction. This gives rise to many side reactions like oxirane ring forming to diol, hydroxyl esters, creation of dimers and oil hydrolysis taking place. Therefore, to overcome these glitches associated while using a strong mineral acid in the epoxidation reaction certain enzymes, resins and catalysts are being used [67-69]

1.7 PRESENT WORK

In present work, to formulate an environmentally friendly bio lubricant castor oil was chosen and various formulations were made using thermal and chemical modifications of castor oil for probable use as a bio-lubricant.

As a first formulation, the castor oil was thermally modified to form thermally modified castor oil (TMCO) for formulating TMCO raw castor oil was heated to 150°C and was maintained at this temperature for a time period of 2 hrs.

As second formulation, castor oil methyl ester (COME) was synthesized using transesterification reaction between castor oil and methanol in order to study the lubricating capacity of methyl esters. Also, it was suggested in some research papers that due to the glycerol content existing within oil, the vegetable oils possess low oxidation stability thus transesterification of castor oil was done to remove glycerol and produce COME that were found out to be giving improved lubricity and oxidation stability.

As a third formulation, the castor oil was chemically modified via; epoxidation to produce chemically modified castor oil (CMCO).In the formulations bio-additive package was also introduced to improve some of the properties .

Finally, all the formulations were exposed to a number of tribological tests such as evaporative loss, viscosity index, iodine value, pour point, oxidation stability and four ball wear test. Results were analysed and compared with conventional synthetic lubricant SAE 20W40. The castor oil based formulations showed promising properties to justify themselves to be an excellent substitute to conventional SAE 20W40 oil.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

Renewable raw materials are going to play a very noteworthy role in the development of sustainable green chemistry. They offer a large number of possibilities for applications which can be rarely met by petro chemistry .Oils and fats of vegetable and animal origin share the greatest proportion of the current consumption of renewable raw materials in chemical industry.

A steady increase in the use of eco-friendly consumer products like lubricants has occurred as a result of strict government regulation and increased public awareness for a pollution free environment .There are wide ranges of lubricant base oils in current use which includes mineral oils, synthetic oils, re-refined oils, and vegetable oils. Among these, mineral oils are the most commonly used. They consist predominantly of hydrocarbons but also contain some sulphur and nitrogen compounds with traces of a number of metals. Due to their inherent toxicity and non-biodegradable nature they pose a constant threat to ecology and vast ground water reserves .Synthetic oils include others polyalphaolefins, synthetic esters and polyalkylene glycols. Polyalphaolefins are petrochemical derived synthetic oils that mostly resemble mineral oils.

Synthetic esters form a large group of products, which can be either from petrochemical or oleo chemical origin. In the preparation of re-refined oil, oil undergoes an extensive re-refining process to remove contaminants to produce fresh base oil. These concerns have resulted in an increasing interest in vegetable oils with high content of oleic acid, which are considered to be potential substitutes to conventional mineral oil-based products.

Vegetable oil lubricants are preferred not only because they are renewable raw materials but also because they are biodegradable and non-toxic .They also acquire most of the properties required for lubricants such as high index viscosity, low volatility and good lubricity and are also good solvents for fluid additives.

However, vegetable oils have poor oxidative and thermal stability, which is due to the presence of unsaturation .This unsaturation, restricts their use as a good lubricant. Several attempts have been made to improve their oxidative stability such as transesterification of trimethylopropane and rapeseed oil methyl ester ;selective hydrogenation of polyunsaturated C=C bonds of fatty acid chains .and conversion of C=C bonds to oxirane ring via epoxidation .Among these, epoxidation received special attention because it opened up a wide range of feasible reactions that can be carried out under moderate reaction conditions due to the high reactivity of the oxirane ring .

2.1 VEGETABLE OILS AS BIO LUBRICANT

Chhibber et al. [70] studied the viability of various vegetable oil deriavatives for use as an environment friendly lubricants and fuels. Fuels, methyl esters can work as highly efficient environment-friendly fuels particularly for applications in passenger transport, light commercial vehicles and generators. Various properties were checked for all the vegetable oil derivatives. Certain modification via epoxidation was also suggested by the study for the improvement of properties such as oxidation stability and pour point.

Nagendramma et al. [71] showed that Synthetic and vegetable oil based esters offer the best choice in formulating environment friendly lubricants. Their studies highlight some recent developments in the area of biodegradable synthetic ester base stocks for formulation of new generation lubricants The developed products found applications in automotive transmission fluids, metal working fluids, cold rolling oils, fire resistant hydraulic fluids, industrial gear oils, neat cutting oils and automotive gear lubricants either alone or in formulations.

Silva et al. [72] studied the production of biodegradable lubricants from vegetable oils via chemical catalysis through chemical modifications of the plant oil. The studies suggested an improvement in the cold flow properties and a great improvement in oxidation stability of the vegetable oil.

Ozioko [73] worked on the possibility of producing bio-lubricant with soybean seeds as a case study. By using Solvent extraction process using normal hexane and analysed Proximate properties such as moisture, volatile matter, ash, fixed carbon content and physical properties such as viscosity, flash/fire point, pour point and density which were compared to commercially available lubricant and discovered that the crude soybean oil sample exhibits a good base as a bio-lubricant.

Bhatia et al. [74] prepared some experimental blends based on jojoba oil and screened them for physico-chemical, wear and scuffing characteristics and found the results to be highly encouraging. The piston-tightening, wear and deposit forming tendencies were also assessed in a short duration engine test. The results showed that jojoba oil has a good potential to replace mineral oil base stocks in two-stroke gasoline engine oil formulations.

Erhan et al. [75] conducted studies on various vegetable oils for their potential use as a lubricant base stock the study was concentrated on oxidative stability and low temperature problems associated with vegetable oils and thin film oxidation test was used to compare oxidative stabilities. The studies found the following:

- “ Oxidative stability of vegetable oils is much lower than mineral oils.
- “ Low temperature performance of vegetable oils is poor as compared to mineral oils.
- “ Chemical modification of triglycerides is necessary to: completely eliminate poly unsaturation (for better oxidative stability)
- It is necessary to find an optimal extent of chemical alteration (improved low temperature behaviour).

2.2 CASTOR OIL AS BIO LUBRICANT

Naik et al. [76] studied the effect of alcohol and catalyst loading on transesterification of castor oil and the optimum condition were identified, which could provide valuable experimental data for future industrial application.in the study. Lipozyme TL-IM was successfully used as a biocatalyst for castor oil transesterification with different alcohol propanol, butanol and iso amyl alcohol under supercritical carbon dioxide to produce castor oil alkyl esters. The Castor Oil Alkyl Ester was found to have enhanced cold flow properties and lubricity.

Erhan et al. [77] conducted studies on oxidation and low temperature stability of vegetable oil-based lubricants. They found that vegetable oils are promising candidates as base fluid for eco-friendly lubricants because of their excellent lubricity, biodegradability, viscosity–temperature characteristics and low volatility but their use is restricted due to low thermo-oxidative stability and poor cold flow behaviour. They conducted exhaustive studies to improve the oxidation behavior and low temperature fluidity of vegetable oil derivatives. Among the various possible avenues found, the combination of chemical additives, diluent (polyalphaolefin), and high-oleic vegetable oils offer the best option for achieving the ultimate goal. Vegetable oil-based lubricants formulated using the above approach were found to exhibit superior oxidative stability, and improved low temperature properties such as pour points compared to commercially available industrial oils such as bio-based hydraulic fluids.

Singh et al. [78] found the use of castor oil based lubricant in reducing Smoky emissions from two-stroke gasoline engines For the study a biodegradable 2T-oil was developed from castor oil, which consisted of tolyl monoesters and performance additives but no miscibility-solvent. Evaluation revealed that on one hand it reduced smoke by 50–70% at 1% oil fuel ratio and on the other hand it was at par with standard product specification. Starting problems, piston-seizer or any other driving problems were not observed during the test.

2.3 ESTERIFIED VEGETABLE OILS AS BIO LUBRICANT

Bokade et al.[79] showed in their experiments the use of different lower and higher alcohols viz; methanol, ethanol, n-propanol and n-octanol, for the synthesis of methyl, ethyl, propyl and octyl fatty acid esters by transesterification of vegetable oil (triglycerides) with respective alcohols also known as ‘Bio-diesel’ and ‘Biolubricants’ was studied in detail.

Petran et al. [80] studied the synthesis of waste cooking oil and fats derived bio lubricant by using simple transesterification process with higher alcohols and found the properties of the produced biolubricant comparable to that of commercially available SAE30 oil.

Naik et al. [81] studied the reactive extraction of castor seed and investigated the feasibility of the reaction to find out optimum reaction conditions. Also castor oil methyl ester was formed using transesterification the study also suggested the potential use of COME as bio lubricants as promising due to its high viscosity, low pour point, and good lubricity. The studies concluded that reactive extraction is a simple, high yielding and cost effective process for the production of methyl esters as bio lubricant.

2.4 EPOXIDISED VEGETABLE OIL AS BIO LUBRICANT

Lathi et al. [82] studied A novel process for the production of biodegradable lubricant-base stocks from epoxidized vegetable oil with a lower pour point via cationic ion-exchange resins as catalysts which involved two steps, first, ring opening reactions by alcoholysis followed by esterification of the resultant hydroxy group in the first step. The ring-opening reaction of epoxidized soybean oil with different alcohols such as n-butanol, iso-amyl alcohol and 2-ethylhexanol was carried out in presence of Amberlyst 15 (Dry) as a catalyst. Pour points of the products were observed this study showed that the introducing branching on epoxidized soybean oils leads to dramatic improvement of low pour point value. The ring opening reaction of epoxidized soybean oils with 2-ethylhexanol gives the low pour point value.

Salimon et al. [83] showed a series of chemically modified biolubricant basestocks derived from ricinoleic acid. The reactions were monitored and products were confirmed by NMR and FTIR. The synthesis protocol were carried out in three stages: (1) epoxidation of ricinoleic acid; (2) synthesis of 10,12-dihydroxy-9-acyloxystearic acid from epoxidized ricinoleic acid; (3) esterification of the acyloxystearic acid The viscosity index, flash point, pour points (PP), and oxidative stability of the resulting products were measured. The resulting esters could plausibly be used as bio-based industrial materials in biolubricants, surfactants, or fuel because they have improved physicochemical properties.

Lathi et al. [84] conducted studies on a novel process for the production of biodegradable lubricant-based stocks from epoxidized vegetable oil with a lower pour point via cationic ion-exchange resins as catalysts. The studies clearly suggested that the epoxidation process led to an improved pour point and oxidative stability.

Patwardhan et al. [85] studied the formation of biolubricant formed from Mahua oil (Madhumica indica) with an iodine value of 88 g/100 g, and containing 46% oleic acid and 12.74% linoleic acid,via epoxidation in situ method with hydrogen peroxide as oxygen donor and glacial acetic acid as active oxygen carrier in presence of catalytic amount of an inorganic acid. Catalytic loading of two different acids, i.e., H_2SO_4 and HNO_3 were studied, and H_2SO_4 was found to be more effective in terms of conversion to oxirane. The effects of various parameters, such as temperature, hydrogen peroxide-to ethylenic unsaturation mole ratio, acetic acid-to-ethylenic unsaturation mole ratio, and stirring speed, on the epoxidation rate as well as on the oxirane ring stability and iodine value of the epoxidised mahua oil (EMO) were studied. The effects of these parameters on the conversion to the epoxidised oil were studied and the optimum conditions were established

Kulkarni et al. [86] studied Epoxidation of mustard oil and ring opening with 2-ethylhexanol for bio-lubricants with enhanced thermo-oxidative and cold flow characteristics

Erhan et al. [87] demonstrated the improved performance of epoxidized soybean oil (ESBO) over soybean oil (SBO) and genetically modified high oleic soybean oil (HOSBO) in certain high temperature lubricant application. The study offers a detailed insight about the thermal, oxidative and frictional behaviour of ESBO as a potential candidate for high temperature lubrication. The deposit-forming tendency of ESBO is significantly reduced due to the removal of multiple unsaturations in fatty acid chains.

2.5 TRIBOLOGICAL TESTING OF BIO LUBRICANTS

Shahabuddin et al. [88].outlined the tribological characteristics of Jatropha oil (JO) contaminated bio-lubricant by using Cygnus wear and Four-ball tribo testing machines. To formulate the bio-lubricants for studies, 10–50% by volume of Jatropha oil was blended with the base lubricant SAE 40. It was found that the addition of Jatropha oil in the base lubricant acted as a very good lubricant additive which reduced the friction and wear scar diameter of maximum 34% and 29%, respectively during the tribo test. The studies extensively suggested the application of 10% bio-lubricant in the automotive engine will enhance the mechanical efficiency and take part to reduce the dependency on petroleum oil as well.

Erhan et al.[89] described the tribo chemical evaluation of vegetable oil based anti-wear additive obtained through chemical modification. Also it was suggested after finding the friction and wear behaviour that thio ether hydroxyl vegetable oil can be used as a bio lubricant.

Kailas et al. [90] studied the effect of oxidation on the tribological performance of few vegetable oils by subjecting the oil samples to accelerated ageing in a dark oven at different temperatures, inducing the oxidation under controlled conditions. The samples were analysed for the changes in viscosity, percentage of free fatty acid, peroxide number and were compared with fresh oils samples. Further tribological property was also evaluated and the observed differences were linked to formation of oxidation products like peroxides, kinetics of the oxidation with reference to ageing temperature.

2.6 GAP IN THE LITERATURE

In the light of exhaustive literature review, the below mentioned gaps can be stated in the literature review:

- Exhaustive studies on use of castor oil as bio-lubricant has not been done.
- The use of esterified castor oil as bio-lubricant has not been explored yet
- The oxidation stability of Bio-lubricants and it's improvement has not been done extensively.

2.6 STATEMENT OF THE PROBLEM

Vegetable oil based lubricants are highly attractive substitute to the petroleum based lubricants because these are environmentally friendly, renewable, non-toxic and completely biodegradable. Vegetable oil based lubricants are preferred not only because of renewability but also because of their excellent lubricating properties such as high viscosity index (i.e., minimum changes in viscosity with temperature), high flash-point, low volatility, good contact lubricity and good solvents for fluid additive.

However, vegetable oil based lubricants have some drawbacks such as poor low temperature properties (pour point), poor oxidation stability and thermal stability (due to the presence of unsaturation.

However, through exhaustive literature review we have come to the conclusion that the problem of very poor oxidation stability of the vegetable oil can be answered through chemical modification of vegetable oil via. Epoxidation, where the unsaturated C=C bonds are converted to oxirane ring increasing the oxidative stability of plant oil. Also in the current work we have made methyl ester to check the lubricating properties of esters.

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CHAPTER 3

MATERIALS AND METHODS

3.0 INTRODUCTION

The world today is facing severe oil crisis and environmental pollution, thus there is a great urgency of developing and applying bio based products as a substitute to mineral oil based products. Rapid industrialization and automation in the last decade has increased the demand of mineral oil based lubricant that will get exhausted in the years to come.

Also in addition to the above fact, the biodegradability of mineral-oil based lubricants is around 25% maximum. About 50% of all lubricants sold worldwide end up in the Environment. Due to extensive use of mineral oil based lubricants, several environmental issues such as surface water and groundwater contamination, Air pollution, soil contamination, agricultural product and food contamination are emerging very rapidly. This has led the researchers to look for plant oil based bio-lubricant as an alternative to mineral oil based lubricant.

Vegetable oils are renewable raw materials that possess certain excellent frictional properties e.g. good lubricity, low volatility, high viscosity index, solvency for lubricant additives, and easy miscibility with other fluids etc.

However, a high degree of multiple C–C unsaturations in the fatty acid (FA) chain of vegetable oils causes poor thermal and oxidative stability. This fact confines their use as lubricants to a modest range of temperature.

In the current work for formulation of bio-degradable lubricants simple transesterification reaction was carried out between crude castor oil (CO) and methanol to form castor oil methyl ester (COME).The following above formulation was made to check the applicability of esters as bio lubricant and to check their lubricity. Also castor oil (CO) was chemically modified via epoxidation to formulate chemically modified castor oil (CMCO) to increase oxidative stability of castor oil.as another formulation to be used as a bio lubricant castor oil was thermally modified through a constant heating process for 2 hrs. To form thermally modified castor oil (TMCO) Also to these formulations bio-additive packages were added to improve some of the properties.

Finally all the formulated bio-lubricants were subjected to various tribological tests viz. evaporative loss, viscosity index, iodine value, pour point, oxidation stability and four ball wear test. Results were analysed and compared with conventional synthetic lubricant SAE 20W40.

3.1 CASTOR (RICINUS COMMUNIS) PLANT

Ricinus communis is a species that belongs to the Euphorbiaceae family and it is commonly known as castor oil plant and Palma Christi as shown in Figure 3.1. This plant originates in Africa but it is found in both wild and cultivated states in all the tropical and subtropical countries of the world. In wild conditions this plant is well-adapted to arid conditions and is able to stand long periods of drought.

Figure 3.1: castor plant and castor seeds

Ricinus communis plants can present precocious, median and delayed cylces [91]. The precocious cycle is that in which flowering occurs about 45 days after sowing. The median cycle presents flowering at an intermediate time between the precocious and delayed cycle, which has a flowering time of 90 to 120 days after sowing.

India is the world's largest producer of castor seed.8 to 8.5 lakh tonnes of castor seed annually and accounts for more than 60% of the entire global production.

Castor is grown especially in arid and semi-arid region. India, China and Brazil accounts for 90% of world production. India is gifted with an ideal climatic condition for castor seed. Castor, planting season is during July or August and harvested around December or January. The seed pods are dried, depodded and brought to the market yards during December or January for trading.

The advantage of castor as a bio-lubricant is that it can withstand long period of drought. The oil content in the seed is nearly 50% of the total weight. It is the only unique oil which has an unusual chemical composition of triglyceride of fatty acid. It is the only source of an 18- carbon hydroxylated fatty acid ricinoleic acid with one double bond.

3.2 CASTOR OIL

Castor oil is extracted from the seeds of Palma Christi. Seeds are having approximately 50% oil. This oil is highly viscous, its coloration ranges from a pale yellow to colourless, it has a soft and faint odour and a highly unpleasant taste.

Castor oil dissolves easily in alcohol, ether, glacial acetic acid, chloroform, carbon sulfide, and benzene. It's made up of triglycerides: 91-95% ricinoleic acid, 4-5% linoleic acid, and 1 2% palmitic and stearic acids.

3.3 APPLICATIONS OF CASTOR OIL

Besides being used as a medicine, castor oil is widely used in the industrial field because of its many properties. In the textile industry, castor oil is used for moisturizing and removal of grease in fabrics, and for the manufacturing of waterproof fabrics. In the steel industry, it is used in cutting oils and lubricants for steel lamination at high temperatures and it is also used in other liquids that are necessary for steel work.

The automotive industry uses castor oil for the production of high performance motor oil and braking fluids. Moreover, it is also employed as a softener in the tanning industry and in the production of fluids for hydraulic devices, artificial leather, varnish, paint, linoleum, insulators, powder, fatty acids, enzymes, as a moisturizer for stationary and insecticides; additionally it can be used as a raw material for the fabrication of plastics.

3.4 FFA OF CASTOR OIL

Vegetable oil is the mixture of number of different triglycerides which are one molecule of glycerol esterified to three molecules of long chain mono-carboxylic acid. The molecular formula of vegetable oil is C_{19} $H_{34}O_2$. Castor oil contains nearly 89% ricinoleic acid.

Thus overall castor oil contains 2 % saturated fatty and 98% unsaturated fatty acid. It's made up of triglycerides: 91- 95% ricinoleic acid, 4-5% linoleic acid, and 1-2% palmitic and stearic acids. The fatty acid composition of the castor oil was 4.90% oleic acid, 0.74% palmitic acid, 4.21% stearic acid, 0.67% linoleic acid, 1.0% linolenic acid, 88.26%ricinoleic acid, and 0.22% others. Fatty acid methyl ester reference standards for gas chromatography analysis, including palmitic, stearic, linolenic, linoleic, oleic, ricinoleic, and heptadecanoic methyl esters, all > 99% pure, were purchased from Arjan Dass & Sons.Khari Wabli New Delhi. Methanol, potassium hydroxide, and all other chemicals used in this study were of analytical grade. Table 3.1 shows the fatty acid composition of castor oil.

Table 3.1 Characteristics of fatty acids in castor oil

S. No.	Name of Fatty Acid	Chemical name of fatty acids	Degree of unsaturation	Chemical Formula	% value
1	Earic	Dhydroxyst	-	-	0.7
2	Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$	1.0
3	Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$	1.0
4	Oleic	Octadecenoic	18:1	$C_{18}H_{34}O_2$	3.0
5	Linoleic	Octadecadienoic	18:2	$C_{18}H_{32}O_2$	4.2
6	Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$	0.3
7	Ricinoleic	Ricinoleic	18:1	$C_{20}H_{38}O_2$	89.5
8	Linolenic	Octadecedienoic	18:3	$C_{18}H_{30}O_2$	0.3
9	Saturated	-	-	-	2.3
10	Unsaturated	-	-	-	97.7

3.5 PHYSICO-CHEMICAL PROPERTY OF CASTOR OIL

The physico-chemical property of castor oil is shown in table below:

Table 3.2 Physico-chemical property of Castor oil

Properties		**Units**	**Castor oil**
Viscosity		cSt at 38 °C	226.82
Density		(kg/m^3,40 °C)	956
Flash point		°C	320
Pour point		°C	-15 to 2
Cloud point		°C	4-10
Cetane number		-	36
Calorific Value		(MJ/kg)	36.20
Oil Content	Seed	Wt. %	40-50
	kernel	Wt. %	50
FFA		wt.%	2.8

3.6 VARIOUS FORMULATIONS OF CASTOR OIL FOR BIO-LUBRICANT

The purpose of current experimental study consists mainly of three folds:

1. To synthesize thermally modified castor oil (TMCO) via. Heating the castor oil at a constant temperature for 2 hrs.
2. To synthesize castor oil methyl ester (COME) as a base stock for bio-lubricant through transesterification reaction of castor oil.
3. Chemical modification of castor oil (CO) via epoxidation to synthesize chemically modified castor oil (CMCO).

3.6.0 Raw castor oil (RCO)

As the raw castor oil is having excellent viscosity and great lubricity naturally its properties were directly analysed and it was also subjected to tribological tests to study the relevancy of raw castor oil (RCO) to be used as a bio lubricant.

3.6.1 Thermally modified castor oil (TMCO)

Thermally modified castor oil (TMCO) was synthesized by constant heating of raw castor oil at 150 °C for 2 hrs.

3.6.2 Castor oil methyl ester (COME)

Castor oil methyl ester (COME) was synthesized through transesterification reaction of castor oil in which castor oil was reacted with methanol in presence of base catalyst. The aim of producing castor oil methyl ester is to check the applicability of esters to be used as a base stock for environment friendly bio lubricant.

Trans-esterification

Esters are normally produced by the transesterification of the waste vegetable oil, algal oil or animal fat as a feedstock. The most commonly used alcohol is methanol or ethanol to produce methyl esters or ethyl esters. It is generally referred as fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE).

To make use of vegetable oils in an effective way it should be converted into esters using a single or a two-step conversion process.

Nowadays, there are four different methods available to reduce the viscosity of vegetable oil, which is detrimental to engine hardware, such as blending of oil with petroleum diesel, pyrolysis (Thermal Cracking), emulsification and transesterification as discussed earlier. The pyrolysis and emulsification methods are producing heavy carbon deposits, in complete combustion, increase of lubricating oil viscosity and undesirable side-products such as aliphatic and aromatic compounds and carboxylic acids. Recently, transesterification has been reported as the most common way to produce esters from vegetable with alcohol, in presence of an acid or base catalyst.

For that a two step transesterification process is discussed below and its flow chart is shown in Fig. 3.2 to make esters from raw oil.

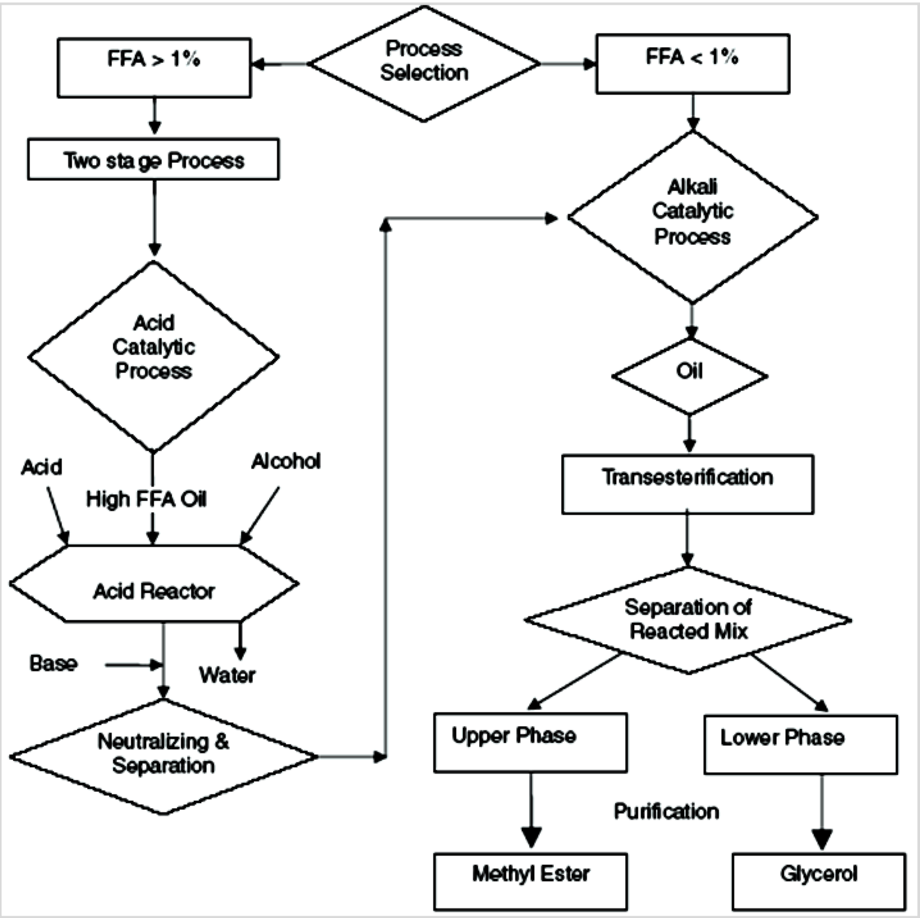
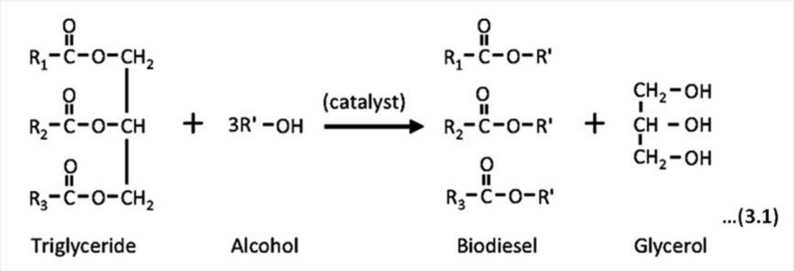


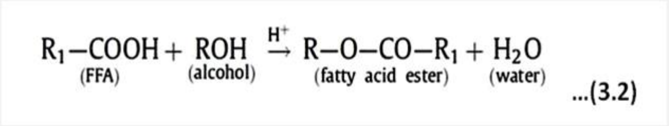
Fig. 3.2: Two step transesterification process

Also the transesterification reaction for FAME is presented in equation (3.1), where R is a mixture of fatty acid chains.



...(3.1)

However, the feed stocks having high content of free fatty acids in the vegetable oil require a different procedure to follow. That is because the free fatty acids do not react with methanol in presence of an alkaline catalyst. However, the FFA can react with alcohol to form ester by an acid-catalysed esterification reaction. This reaction is very useful for handling oils or fats with high FFA, as shown in the equation (3.2) below:



$$\underset{\text{(FFA)}}{R_1{-}COOH} + \underset{\text{(alcohol)}}{ROH} \overset{H^+}{\rightarrow} \underset{\text{(fatty acid ester)}}{R{-}O{-}CO{-}R_1} + \underset{\text{(water)}}{H_2O} \quad \text{...(3.2)}$$

Normally sulphuric acid is considered as the suitable catalyst for this reaction, however a good range of acids may be considered for the same purpose. Therefore, vegetable oil feedstock's have more than 2% free fatty acid contents are generally transesterified in two stages. In the first stage the FFA is reacted with the alcohol in presence of acid catalyst and when the FFA is reduced below 2%, then it is transesterified in presence of alkaline catalyst.

Trans esterification reaction

In current research we carried out transesterification by reacting castor oil with methanol in the presence of a basic catalyst (NaOH). Castor oil was supplied by Arjan Dass & Sons.Khari Wabli, New Delhi and the castor oil methyl ester (COME) was processed in a batch type reactor. The catalyst was dissolved into the alcohol by vigorous stirring in a small reactor. The oil was transferred into the reactor and then the catalyst/alcohol mixture was poured into the oil and the final mixture stirred vigorously for two hours. Two phases were obtained at the end of the reaction: ester and crude glycerol. Castor oil methyl ester (COME) was observed in the top one and glycerine, a sub product of the process, was observed in the lower one. Since the castor oil used as a raw material presented some humidity (0.2%) soaps became present but they were removed by a washing process.

3.6.3 Chemically modified castor oil (CMCO)

From the exhaustive literature review and studies it was found that the vegetable oil based lubricants possessed excellent lubricity and viscosity index but they possessed very poor oxidation stability due to a number of unsaturations present in the vegetable oils. Thus to increase the oxidation stability of raw castor oil (RCO) it was chemically modified via epoxidation to synthesize chemically modified castor oil (CMCO).

Epoxidation

vegetable oil based lubricants have some drawbacks such as poor low temperature properties (pour point), poor oxidation stability and thermal stability (due to the presence of unsaturation) [92].However, low temperature properties of vegetable oil based lubricants can be attenuated with the use of additives [93].The oxidative stability of the vegetable oil based lubricants can be improved by selective hydrogenation of polyunsaturated C=C bonds of fatty acid chain [94] or conversion of C=C double bonds to oxirane ring via epoxidation [95-96].A wide range of reactions can be carried out under moderate reaction conditions by modification of C=C double bonds to oxirane ring [97] and hence, it received more attention as compared to hydrogenation of C=C double bonds and hence in the current work also we did epoxidation reaction to increase the oxidative stability of plant oil.

Epoxidation of fatty acid is a reaction of C=C with active oxygen which results in the addition of an oxygen atom, converting the original double bond into a three membered epoxide oxirane ring [98].

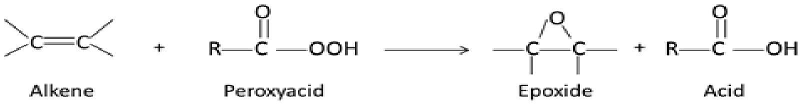


Figure 3.3 ***epoxidation reaction***

Epoxidised vegetable oil is produced industrially by in situ epoxidation process, in which acetic or formic acid reacts with hydrogen peroxide in the presence of mineral acid such as sulphuric or phosphoric acid[99]. However, use of strong mineral acid leads to many side reactions, such as oxirane ring opening to diol, hydroxyl esters, dimer formation and also hydrolysis of oil. Enzymes, resins and heterogeneous catalysts are being used for the epoxidation of oil to overcome the problems connected with the use of mineral acids [100-102].

Epoxidation reaction

The Epoxidation reaction was carried out in a fully baffled mechanically agitated contactor made of glass (6.5 cm i.d. and 250 ml capacity), equipped with a 2 cm diameter six-bladed glass disk turbine impeller, and reflux condenser. The contactor assembly was immersed in a thermostatic water bath, with temperature control ±10°C. The epoxidation method reported by Swern (1949) was used [103].

The required amount of raw castor oil (RCO) was placed in the contactor and suitable amount of acetic acid and sulphuric acid were added, and the mixture was stirred for 45 min. Then 12.5 g of 30% aqueous hydrogen peroxide was added drop-wise at a rate such that it was completed in an hour and the reaction was continued further for 4 hours. The collected sample was then extracted with diethyl ether, washed with water until it was made acid free.

3.7 DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES AND TRIBOLOGICAL TESTS

3.7.0 Equipment

The following equipment's were used in the laboratory for determination of Physico-chemical properties and tribological evaluation of the various formulated vegetable oil based lubricants. These are used in CASRAE research centre of Delhi Technological University, Delhi.

3.7.1 Density meter

Density meter used in laboratory is DMA 4500AntoParr model. This density meter works on the principle of oscillating U-tube. The oscillating U-tube is a technique to determine the density of liquids and gases based on an electronic measurement of the frequency of oscillation, from which the density value is calculated. This measuring principle is based on the Mass-Spring Model.

The sample is filled into a container with oscillation capacity. The Eigen frequency of this container is influenced by the sample's mass. This container with oscillation capacity is a hollow, U-shaped glass tube (oscillating U-tube) which is electronically excited into undamped oscillation (at the lowest possible amplitude). The two branches of the U-shaped oscillator function as its spring elements.

The direction of oscillation is normal to the level of the two branches. The oscillator's Eigen frequency is only influenced by the part of the sample that is actually involved in the oscillation. The volume involved in the oscillation is limited by the stationary oscillation knots at the bearing points of the oscillator. If the oscillator is at least filled up to its bearing points, the same precisely defined volume always participates in the oscillation, thus the measured value of the sample's mass can be used to calculate its density.

Plate 3.1: Density Meter

3.7.2 Kinematic viscometer

Viscosity is an important property of fuel and it can be defined as measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. In general too viscous fuel tends to form scum and deposits on cylinder walls, piston head etc., and cause atomization problems. So it is desirable that viscosity of fuel should be low. The different blend samples are prepared are investigated for viscosity at 400 C using a kinematic viscometer as per the specification given in ASTM D445. It consists of a capillary tube in which sample to be test is filled. The capillary tube has two marks engraved on it. The time for flow of fuel sample from upper mark to lower mark is measured and kinematic viscosity is calculated using time taken by each sample. The plate of the kinematic viscometer apparatus is shown below.

The kinematic viscosity of different fuel blends can be calculated as:

$\upsilon = k \times t$

Where,

υ= kinematic viscosity of sample;

k = constant for viscometer;

t = time taken by the fluid to flow through capillary tube

The viscosity index can be calculated using the following formula:

$$V = 100\frac{(L-U)}{(L-H)}$$

Where V indicates the viscosity index, U the kinematic viscosity at 40 C (104 F), and L & H are various values based on the kinematic viscosity at 100 C (212 F) available in ASTM D2270

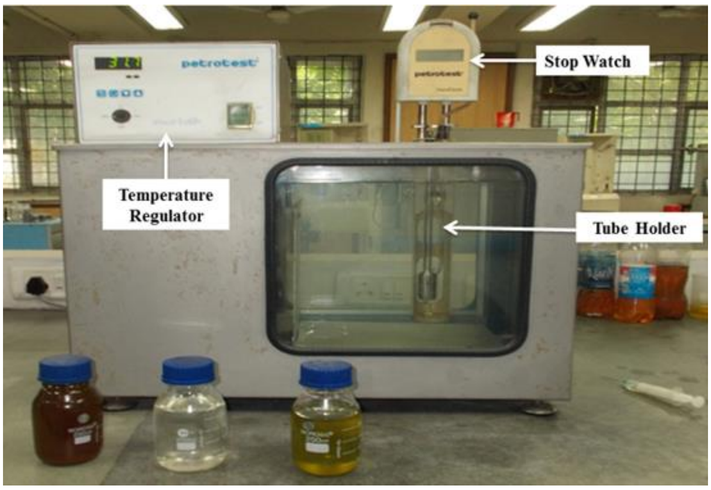


Plate 3.2: Kinematic Viscometer

3.7.3 Flash and fire point

Flash point is the minimum temperature at which the oil vapour, which when mixed with air forms an ignitable mixture and gives a momentary flash on application of a small pilot flame. The flash and fire point of the test fuels were measured as per the standard of ASTM D 93. The sample was heated in a test cup at a slow and constant rate of stirring for proper and uniform heating. A small pilot flame was directed into the cup though the opening provided at the top cover at the regular intervals. The temperature at which these vapour catches flash is observed and called as the flash point of that liquid. Fire point is an extension of flash point in a way that it reflects the condition at which vapour burns continuously for at least for 5 seconds. Fire point is regularly higher than the flash point by 5-8°C.

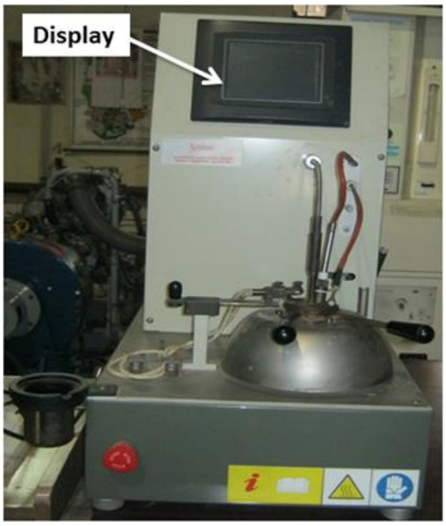


Plate 3.3: Pensky marten flash point apparatus

3.7.4 Gas chromatograph

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, column length and the temperature.

In a GC analysis, a known volume of gaseous or liquid analyte is injected into the "entrance" (head) of the column, using a micro syringe (or, solid phase micro extraction fibres, or a gas source switching system). As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column.

The instrument present here is equipped with a FID (flame ionization detector), enabling us to quantify the quantities of various organic compounds present in the sample being tested. Hence, we can find out precisely the percentage of different fatty acid present in the oil.

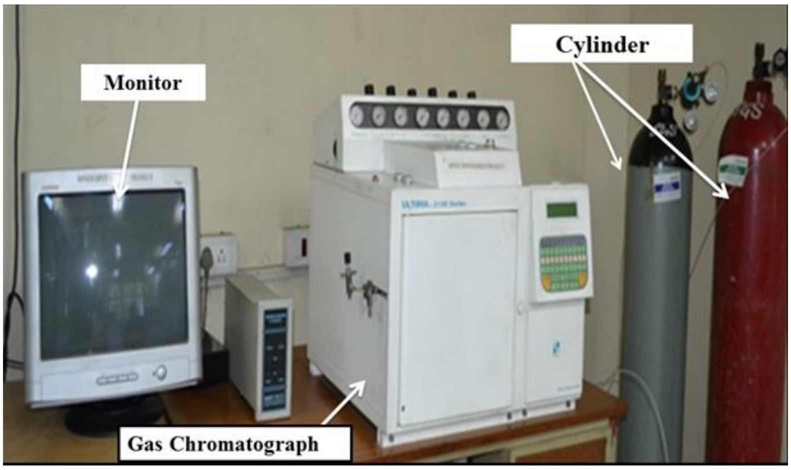


Plate 3.4: Gas Chromatograph

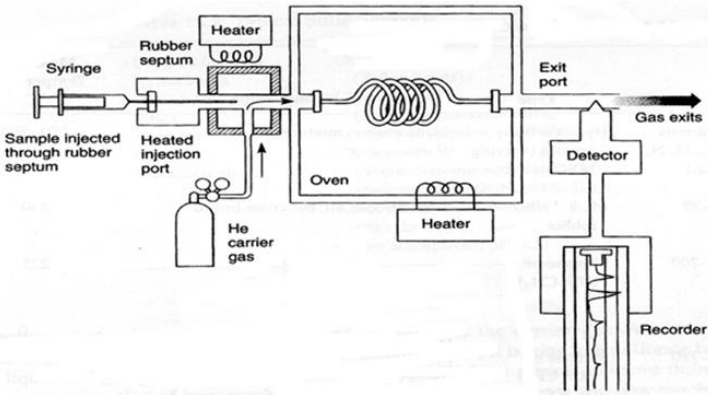


Fig.3.4: Schematic diagram of gas chromatograph

3.7.5 Four ball wear test

To study the resistance to wear characteristics of the formulated bio-lubricant, ASTM D4172 Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method) was chosen. Four Ball-Tests is used to measure the Anti-Wear (AW) and Extreme Pressure (EP) properties of greases and lubricating oils. The point contact interface is obtained by rotating a 12.7mm diameter steel ball under load against three stationary steel balls immersed in the lubricant. The speed of rotation, normal load, and temperature can be adjusted in accordance with published ASTM standards. To evaluate the anti-wear characteristics of lubricants, the subsequent wear scar diameters on the balls is measured. To evaluate the Extreme-Pressure (load-carrying) capacity of lubricants, the normal load at which welding occurs at the contact interface is measured. The test parameters for the above mentioned wear test is shown in table 3.3.

Table 3.3: test parameters according to ASTM D 4172

TEST PARAMETERS	
Speed (rpm)	1200 (±50)
Temperature (°C)	75 (±1.7)
Load (kgf)	40 (±0.2)
Duration (min)	60 (±1)

Table 3.4: test specimen

TEST SPECIMEN	
Ball Material	Steel AISI-E52100
Hardness (HRc):	64-66
Grade	25EP

According to ASTM D4172 test methods, Three 1⁄2in. (12.7-mm) diameter steel balls are clamped together and covered with the lubricant to be evaluated. A fourth 1⁄2in. diameter steel ball, referred to as the top ball, is pressed with a force of 40 kgf (392 N) into the cavity formed by the three clamped balls for three-point contact. Then the top ball is rotated at 1200 rpm for 60 min. Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls. The four-ball wear-test method can be used to determine the relative wear-preventing properties of greases under the test conditions.

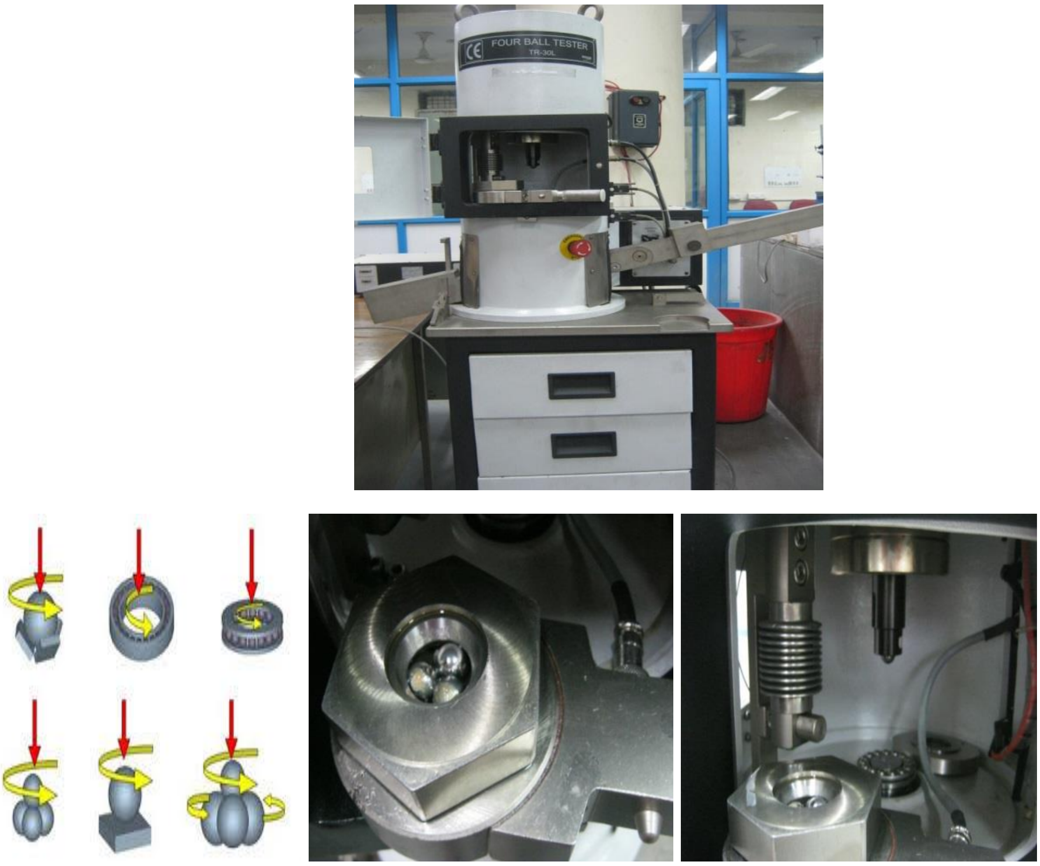


Plate 3.5: four ball wear tester

3.7.6. Evaporative loss test (NOACK Volatility Test)

The evaporation loss is of particular importance in engine lubrication. Where high temperatures occur, portions of oil can evaporate. Evaporation may contribute to oil consumption in an engine and can lead to a change in the properties of oil. Many engine manufacturers specify a maximum allowable evaporation loss. Some engine manufacturers, when specifying a maximum allowable evaporation loss, quote this test method along with the specifications. Procedure, using the Selby-NOACK apparatus, also permits collection of the volatile oil vapours for determination of their physical and chemical properties. Elemental analysis of the collected volatiles may be helpful in identifying components such as phosphorous, which has been linked to premature degradation of the emission system catalyst.

Standard Test Method for Evaporation Loss of Lubricating Oils is experimentally found by the NOACK Method.

The NOACK Volatility Test, otherwise known as ASTM D-5800, determines the evaporation loss of lubricants in high-temperature service. The more motor oils vaporize, the thicker and heavier they become, contributing to poor circulation, reduced fuel economy and increased oil consumption, wear and emissions.

According to ASTM D5800 test method for evaporative loss or volatility test for lubricating oils is conducted on K44001 NOACK Evaporation Loss Analyser A quantity of 65g of a lubricant is placed in an evaporative crucible and heated to 250°C for 60 minutes. The evaporation loss tendencies of the lubricant are determined by passing a constant air stream over the heated sample by means of a vacuum pump.

Plate 3.6: K44001 Noack Evaporation Loss Analyzer and Accessories

Table 3.5: specifications of K44001 NOACK Evaporation Loss Analyser

Conforms to the specifications	ASTM D5800
Capacity:	1 sample
Temperature Range	150°C to 350°C
Temperature Accuracy	±0.1°C
Electrical Requirements	115V 60Hz, 12.0A 230V 50Hz, 5.8A
Dimensions (lxwxh) in.(cm)	23.25x14.5x26.75 (59x36.8x68)
Net Weight	59 lbs (26.7kg)
Required Accessories	Glassware Set, consisting of (2) bottles with ground stoppers, glass tubes, and tubing set ; Vacuum Pump , Evaporation Crucible ; Crucible Wrench and Clamp Reamer, 2mm diameter ; 5 Test Balls, 3.5mm diameter ; Protection Gloves;300g Woods Metal and Brush ; Stand with Inclined Manometer (range: 0-30mm H2O) and Bleed Valve for Manual Regulation of Air Stream

3.7.7. Iodine value test

The iodine value of any vegetable oil product is an indication of the amount of unsaturation present in that oil product and thus shows the degree of easiness with which oxidation of that fatty acid is going to take place. Iodine value is a measure of the quantity of unsaturated bonds i.e. C=C present in the oil. Low values of iodine value represent a high degree of saturation present in the oil. This value gives a clear idea about the possible deposits in the combustion chamber, about storage capacity of oil, about its tendency to polymerize and about the chances of contrary effects on lubricating oil.

In the current experimental study, Lubrizol Test Procedure TP-AATM-112-01 was used to find out the iodine value of the oil sample.

Description of method

The iodine value method is reproducible only if the exact conditions of the test are carefully followed. Any changes in strength of reagent, sample size or reaction time may produce varying results.

The exact specified weight of the sample is accurately weighed into a glass stoppered iodine flask, and dissolved in chloroform. The measured volume of Hanus reagent is accurately added and after thorough mixing, is placed in the dark for exactly one hour. A corresponding reagent blank is simultaneously prepared.

At the end of the specified time, the reaction is stopped by adding potassium iodide and diluting with water to prevent loss of the free iodine. The amount of iodine present is determined by titrating with sodium thiosulfate using starch indicator. The difference between a reagent blank titration and the titration of the test sample represents the amount of iodine absorbed by the sample. The iodine value is calculated as grams of iodine per 100 grams of sample.

Hanus reagent is a solution of iodobromide in concentrated acetic acid. The iodine combines with double bonds slowly under these conditions. A large excess of the halogens must be present to complete the reaction. At the end of the reaction the unconsumed iodine should be greater than 60% of the total. If the sample titration is less than 60% of the blank titration, take a smaller sample and repeat the analysis.

Apparatus

- Iodine flasks, 250 ml. glass stoppered
- 50 ml. Burette with a tolerance of ±0.07 ml
- 25 ml Class A volumetric pipette with a tolerance of ±0.07 ml or appropriate dispenser
- Dispensing device capable of dispensing 10 ml (±1%)
- Dispensing device capable of dispensing 20 ml (±1%)

- Graduated cylinder capable of containing 100 ml
- Analytical balance capable of weighing to the nearest 0.1mg
- Dispensing device capable of dispensing 3 ml

Reagents and solutions

- Chloroform, A.R.
- Hanus Solution, A.O.A.C.
- Potassium Iodide - 10% solution
- Stabilized starch solution - commercially prepared
- Sodium thiosulfate, 0.1N - commercially prepared or AATM 1004

Procedure

- Accurately weigh the sample into a tared 250 ml iodine flask. Determine the sample size from the following table. Accurately record weight to the nearest mg.
- Anticipated Iodine Value Sample Size

0 - 30 0.8 ± .01 g

30 - 50 0.5 ± .01 g

50 - 100 0.25 ± .01 g

100 - 150 0.16 ± .01 g

- Using the dispensing device, add 10 ml chloroform. Dissolve by swirling (NOTE: 50% aqueous products will not dissolve completely until Hanus solution is added).
- Accurately add 25.0 ml Hanus solution and stopper immediately. Swirl to mix thoroughly and place in the dark.
- Simultaneously prepare a corresponding reagent blank containing 10 ml chloroform and 25 ml Hanus solution. Stopper immediately and place the flask in the dark with the test sample.
- After 60 minutes, using the dispensing device, add 20 ml 10% potassium iodide.
- Add by graduated cylinder, 100 ml water rinsing the neck and side walls of the flask during addition of the water.

- Immediately titrate the solution using 0.1N sodium thiosulfate until the aqueous layer's colour begins to lighten.
- Using the dispensing device, add approximately 3 ml starch solution and continue titrating until the blue colour of the aqueous layer begins to disappear.
- Towards the end of the titration, at intervals, stopper the flask and shake vigorously to extract any iodine remaining in the chloroform layer.
- When the end point appears to have been reached, again stopper and shake vigorously, allow the layers to separate and add two drops of starch solution to verify that no blue colour is formed in the aqueous layer.
- Read the burette accurately to two decimal places. Record.

Calculations

$$\text{Iodine Value} = \frac{(\text{ml blank - ml sample}) \times \text{N sodium thiosulfate} \times 12.69}{\text{g sample}}$$

3.7.8 Pour point

If oil is cooled, it will start solidifying at some temperature. This temperature is known as cloud point. This cloudiness or haziness of the oil interferes with its flow at low temperatures. The pour point is that temperature just above which the oil sample will not flow under certain prescribed conditions. This temperature is largely determined by the wax content of the oil since as the temperature is reduced was crystallizes out in long needle shaped crystals, forming honeycomb with oil held in the voids between the crystals.

Generally oil derived from paraffinic crudes tends to have higher pour points than those derived from naphthenic crudes. The pour point can, however be lowered by the addition of a pour point depressant usually a polymerized phenol or ester. These substances function by depositing insulating films on the wax crystals as they began to separate out from the oil and by reducing the size of the crystals.

This characteristic of oil is very important at low temperature operations since it will affect the flow in the pressure line of the lubricating system. Pour point must be at least 15 °F lower than the operating temperature to ensure maximum circulation even at this temperature the oil may be quite viscous so that high power may be necessary for starting.

In the current experimental study ASTM D97 test method for finding out pour point of petroleum products was utilised.

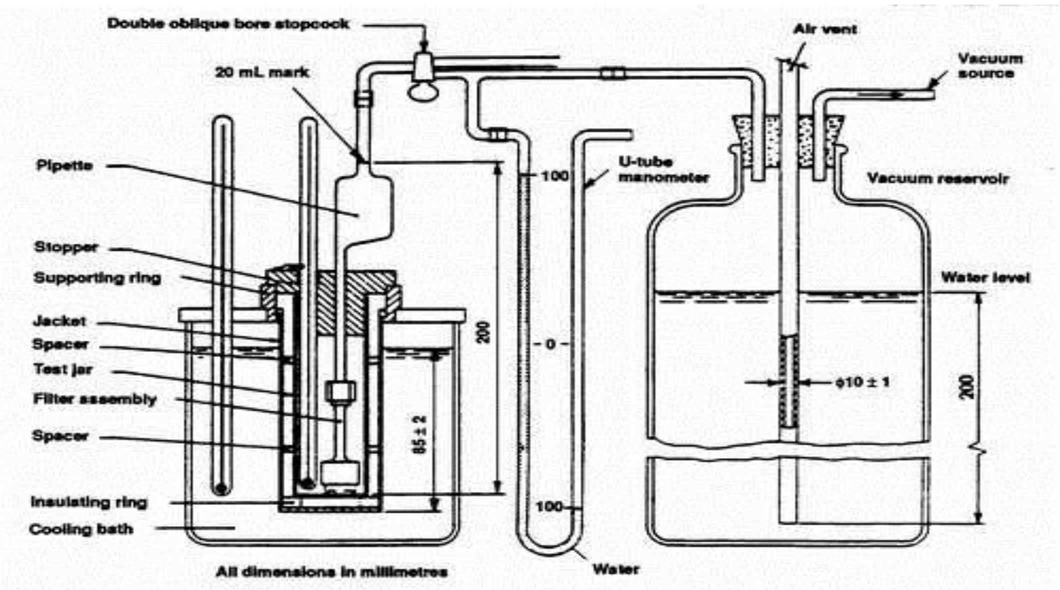


Figure 3.5: schematic of pour point apparatus

Plate 3.7: cloud point and pour point apparatus

3.7.9 Rotating bomb oxidation test

Oxidation stability is a chemical reaction that occurs with a combination of the lubricating oil and oxygen. The rate of oxidation is accelerated by high temperatures, water, acids and catalysts such as copper. The rate of oxidation increases with time. The service life of a lubricant is also reduced with increases in temperature. Oxidation will lead to an increase in the oil's viscosity and deposits of varnish and sludge.

The rate of oxidation is dependent on the quality and type of base oil as well as the additive package used. Some synthetics, such as polyalphaolefins (PAO), have inherently better oxidation stability than do mineral oils. This improved oxidation stability accounts for the slightly higher operating temperatures that these synthetic oils can accommodate.

Generally, oxidation will reduce the service life of a lubricant by half, for every 10°C (18°F) increase in fluid temperature above 60°C (140°F). This concept is based on the Arrhenius rate rule, which is named for the 19th-century Swedish chemist Svante Arrhenius.

Oxidation stability of oil is its resistance to oxidation. Due to oxidation the oil will form deposits on the piston rings and will lose its lubricating property. The products of oxidation vary widely according to the type of oil and the temperature reached which includes carbon, sludge and organic acids which can be corrosive to certain metals thus the oxidation stability of lubricating oils should be as high as possible to reduce the possibility of deposits in the engine.

The most common test to measure the oxidation stability of the oil is the rotating pressure vessel oxidation test (RPVOT) - ASTM D2272, formerly called the rotating bomb oxidation test (RBOT). In essence, the test involves placing a sample of oil into a pressure vessel along with a ration of water and a copper coil. The vessel is pressurized to 90 psi with pure oxygen and placed in a heating bath set at 150°C on a device that rotates at 100 rpm. As the temperature of the pressure vessel and its content increases, the pressure increases. The point at which it stabilizes is defined as T_0, which represents the start of the test. Over time, the oil’s ability to resist oxidation degrades as a result of stress-induced additive depletion, to the point where the base oil starts to react with the oxygen as the oil molecules begin to oxidize. Because the oxygen is being incorporated into the oil’s chemistry, the pressure within the sealed pressure vessel begins to drop. The point at which the pressure drops by 25 psi from the pressure at T_0 defines the termination of the test, denoted as T_1. The time, in minutes, required to go from T_0 to T_1, is reported as the oil’s RPVOT value (Figure 3.9).

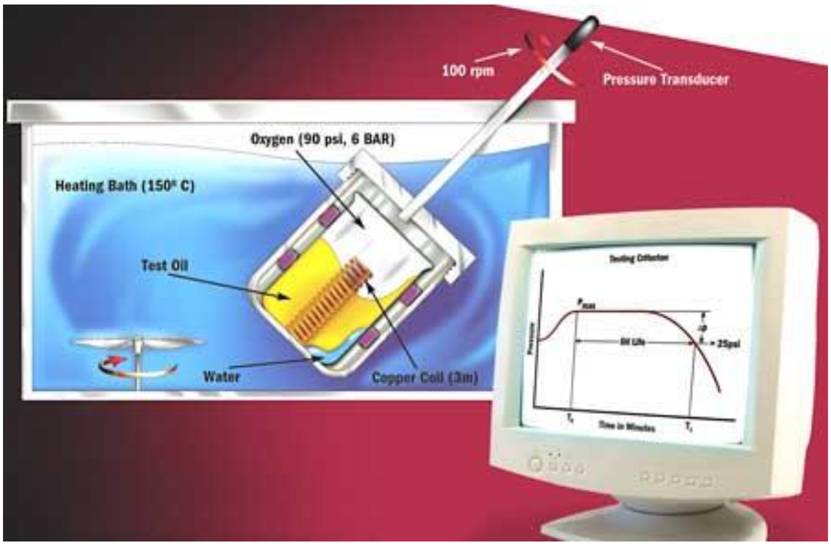


Figure 3.6: rotating bomb oxidation test

Plate 3.8: RBOT test apparatus

CHAPTER 4

RESULTS AND DISCUSSION

4.0 INTRODUCTION

In recent years, worldwide concern about the environmental issues and energy savings are demanding an urgent need for development in research to discover increasingly advanced lubricants as the alternatives to mineral base oils, a non-renewable natural source [104]. Lubricants are used in all aspects of manufacturing industry, transport and domestic life such as in automotive, aviation, metalworking and refrigeration. Among the most used lubricants, the engine oils of automotive industry are the most important. The alternatives to conventional engine oil must be environmentally acceptable, economically improved, excellent low-temperature fluidity and cold starting, high-temperature oxidation resistance, renewable and technically feasible [105]. Many of these basic requirements are satisfied by Biolubricant that could be derived from various plant oils sources by chemical modification. Biolubricant has many advantages over mineral oil such as being renewable with higher lubricity, viscosity indices, shear stability, dispersancy, lower volatility and biodegradable which decreased environmental hazards [106].

Plant oils will compete for a share of the emerging Biolubricants market with mineral oil-based lubricants based on a number of market reports [107–109]. Several studies showed the improved performance of the chemically modified vegetable oil-based synthetic esters for lubrication purposes [110–115]. The native oils have obviously some drawbacks such as poor oxidative stability, sensitivity to hydrolysis and low-temperature fluidity [116]

Thus in the present experimental study various formulations of castor oil were formulated to check the applicability as bio-lubricant.

4.1 Raw castor oil (RCO)

As the raw castor oil is having excellent viscosity and great lubricity naturally its properties were directly analysed and it was also subjected to tribological tests to study the relevancy of raw castor oil (RCO) to be used as a bio lubricant.

4.2 Thermally modified castor oil (TMCO)

Thermally modified castor oil (TMCO) was synthesized by constant heating of raw castor oil at 60°C for 2 hrs.

4.3 Castor oil methyl ester (COME)

Castor oil methyl ester (COME) was synthesized through transesterification reaction of castor oil in which castor oil was reacted with methanol in presence of base catalyst.the aim of producing castor oil methyl ester is to check the applicability of esters to be used as a base stock for environment friendly bio lubricant.

4.4 Chemically modified castor oil (CMCO)

From the exhaustive literature review and studies it was found that the vegetable oil based lubricants possessed excellent lubricity and viscosity index but they possessed very poor oxidation stability due to a number of unsaturations present in the vegetable oils. Thus to increase the oxidation stability of castor oil (RCO) it was chemically modified via epoxidation to synthesize chemically modified castor oil (CMCO).

Finally all the formulated bio-lubricants were subjected to various tribological tests viz. evaporative loss, viscosity index, iodine value, pour point, oxidation stability and four ball wear test. Results were analysed and compared with conventional synthetic lubricant SAE 20W40.

4.5 RESULTS OF VARIOUS PHYSICO-CHEMICAL AND TRIBOLOGICAL TESTS

4.5.0 Evaporative losses

The lubricant base stocks are chosen by considering evaporative losses as one of the most important property. The NOACK volatility (ASTM D 5800) test is used to determine the evaporative losses of motor oil at high temperatures.

According to ASTM D5800 test method for evaporative loss or volatility test for lubricating oils is conducted on K44001 NOACK Evaporation Loss Analyser. A quantity of 65g of a lubricant is placed in an evaporative crucible and heated to 250°C for 60 minutes. The evaporation loss tendencies of the lubricant are determined by passing a constant air stream over the heated sample by means of a vacuum pump.

Figure 4(a) demonstrates that all the vegetable based bio-lubricant shows lower evaporative loss than commercially available SAE 20W40 oil, this might be due to the fact that the size of the molecules in vegetable oils are highly consistent.

Raw castor oil (RCO) based bio-Lubricant shows very low evaporative loss of 0.09% by weight as compared to that of SAE 20W40 which is found to be 3.07% where as for TMCO,COME,CMCO bio-Lubricant formulations were 0.07%, 0.16% & 0.19% respectively. Lower oil consumptions are one of the major benefits of lower evaporative losses.

The NOACK Volatility Test, otherwise known as ASTM D-5800, determines the evaporation loss of lubricants in high-temperature service. The more motor oils vaporize, the thicker and heavier they become, contributing to poor circulation, reduced fuel economy and increased oil consumption, wear and emissions.

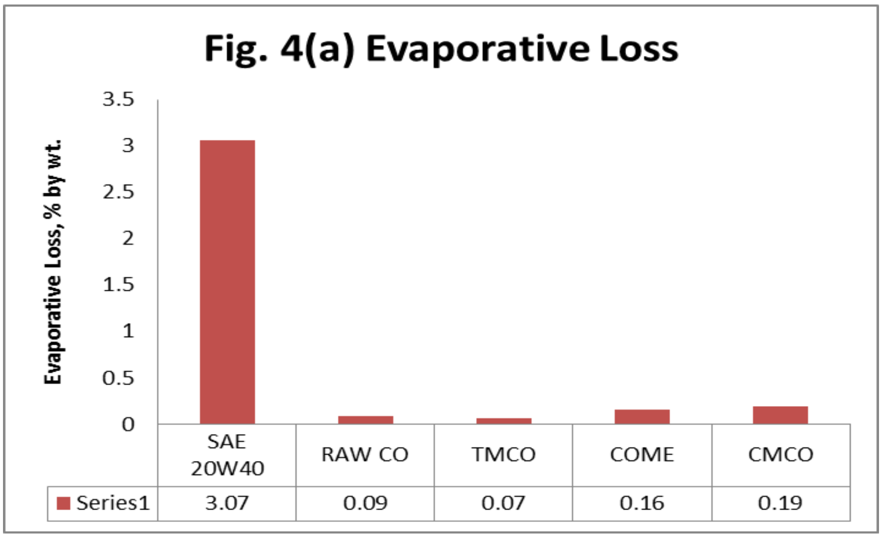


Figure 4(a): variation of evaporative losses, % by wt. for various formulations

4.5.1 Viscosity Index

Viscosity and VI are among the most important physical properties of any lubricant. Viscosity mainly controls the hydrodynamic behaviour of lubricants. Viscosity of oil is essentially a measure of the oil resistance to shear. It is the friction between lubricant molecules or internal resistance to flow. High viscosity implies high resistance to flow. Viscosity varies inversely with temperature, is also affected by pressure and, in some cases, by the shear rate.

Viscosity is commonly measured as shear stress and shear rate, or as the time required for an oil sample to flow through a standard orifice at a given temperature. Viscosity measured directly by shear, referred to as the dynamic viscosity η, is expressed in centi Poise (1 cP = 1 mPa s). The oil industry usually employs kinematic viscosity ν (dynamic viscosity divided by oil density), expressed in centiStokes (1 cSt = 1 mm2/s), conventionally at 40 and 100 °C. The kinematic viscosity values (at 40 °C) are at the basis of the ISO grades for lubricating oils for industrial use.Viscosity as measured in time is expressed in SUS at 100 °F and 210 °F.

Lubricant viscosity is a crucial property in application. Too high a viscosity of the lubricant for a given load means an excessive hydrodynamic film thickness, which translates into a waste of energy in shearing the thick film, heat development, and accelerated lubricant decomposition and mechanical failure of the surfaces. At too low a viscosity the system will operate in the boundary lubrication regime, leading to energy waste in overcoming high frictional forces, wear of metal components and reduced equipment lifetime.

VI is an arbitrary, dimensionless number which expresses the resistance of a lubricant to viscosity change with temperature. It is therefore considered a good indicator of the useful temperature range of a lubricant. Before the emergence of synthetic oil, the Dean and Davis viscosity index, defined as a function of Saybolt Universal viscosities of an oil at 100 °F and 210 °F, was on a scale of 0 to 100 [87]. With the advent of synthetic oils and additives, the scale now ranges from negative values to over 200 (super high VI), but VI still remains as an indicator of quality. Lubricating oil with high VI displays only small changes in viscosity with temperature, which denotes stable viscosity. The higher its VI value, the greater the resistance of a lubricant to thicken at low temperatures and thin out at high temperatures. The VI of oil is crucial in selecting a lubricant for a given application.

Lubricating oil must maintain a sufficient viscosity at high temperature and still should not be too viscous for starting the engine at low temperatures. Figure 4(b) shows the values of viscosity index of different oils. CMCO based bio-Lubricant shows highest viscosity index of 194.28 as compared to that of SAE 20W40 which is found to be 133 whereas for RCO,TMCO & COME based bio-Lubricants were189, 184.62 & 171 respectively. The unique structure of vegetable oils having a high order consistency in molecular weight can be the major reason behind this. This unique molecular interface of vegetable oil also leads to oil having high VI.

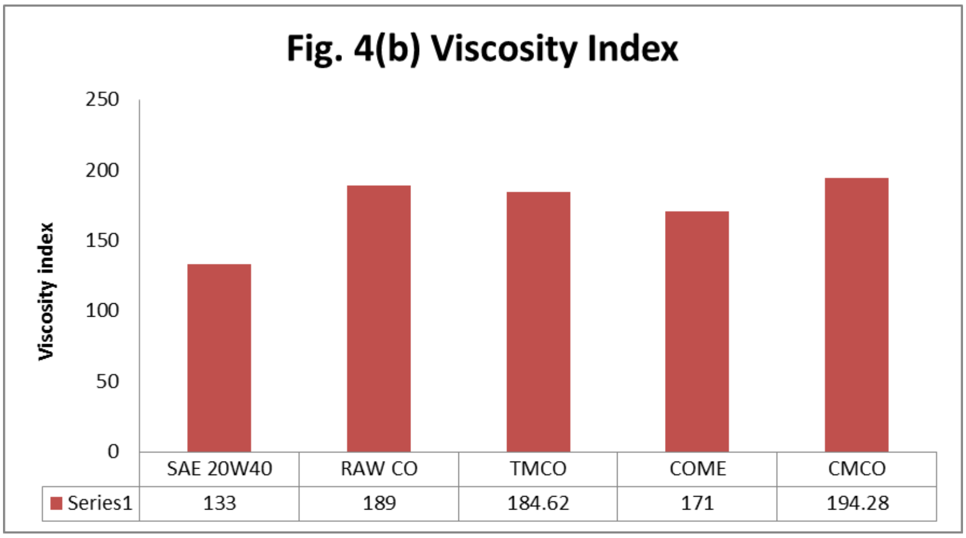


Figure 4(b): variation of viscosity index of various formulations

4.5.2 Iodine value

Iodine value, also called Iodine Number, in analytical chemistry, measure of the degree of unsaturation of oil, fat, or wax; the amount of iodine, in grams, that is taken up by 100 grams of the oil, fat, or wax. Saturated oils, fats, and waxes take up no iodine; therefore their iodine value is zero; but unsaturated oils, fats, and waxes take up iodine. (Unsaturated compounds contain molecules with double or triple bonds, which are very reactive toward iodine.) The more iodine is attached, the higher is the iodine value, and the more reactive, less stable, softer, and more susceptible to oxidation and rancidification is the oil, fat, or wax. In performing the test, a known excess of iodine, usually in the form of iodine monochloride, is allowed to react with a known weight of the oil, fat, or wax, and then the amount of iodine remaining unreacted is determined by titration.

The iodine value of any vegetable oil product is an indication of the amount of unsaturation present in that oil product and thus shows the degree of easiness with which oxidation of that fatty acid is going to take place. Iodine value is a measure of the quantity of unsaturated bonds i.e. C=C present in the oil. Low values of iodine value represent a high degree of saturation present in the oil. This value gives a clear idea about the possible deposits in the combustion chamber, about storage capacity of oil, about its tendency to polymerize and about the chances of contrary effects on lubricating oil.

In the current experimental study, Lubrizol Test Procedure TP-AATM-112-01 was used to find out the iodine value of the oil sample. The iodine values of formulated bio-Lubricants were shown in figure 4(c). Iodine values were determined to be relatively higher in the case of TMCO,COME & RCO based bio-lubricants, which were found to be 86.22 g/100g, 74.32 g/100g, 88.93 g/100g respectively than with SAE 20W40 which was found to be nil. The iodine value of CMOPO was found to be 4.2 g/100g which shows the effect of epoxidation leading to removal of unsaturation.

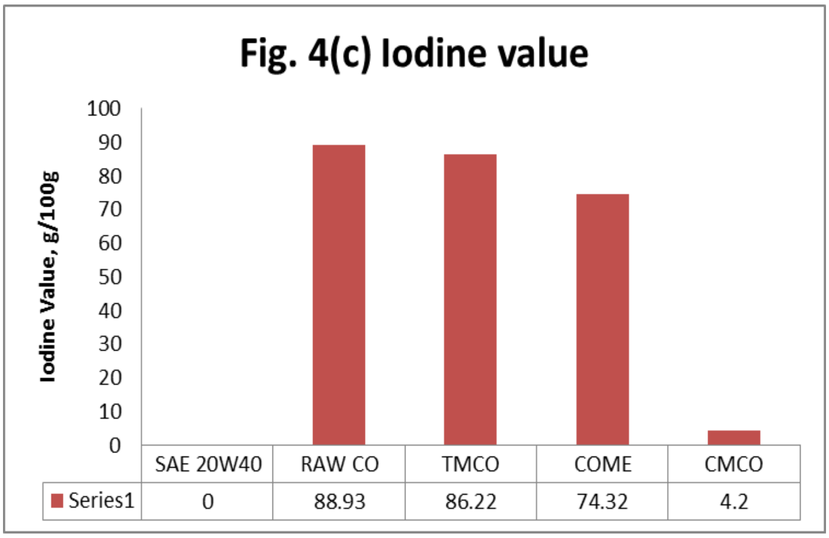


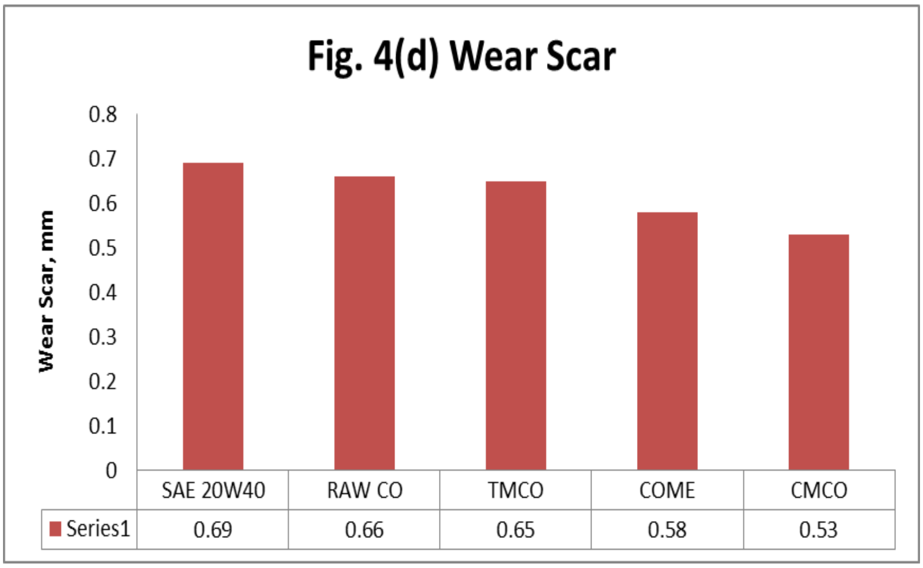
Figure 4(c): variation of iodine value,g/100g for various formulations

4.5.3 FOUR BALL WEAR TEST

An anti-wear property of lubricant was evaluated by measuring the mean wear scar diameter as per ASTM D 4172. According to ASTM D4172 test methods, Three 1⁄2in. (12.7-mm) diameter steel balls are clamped together and covered with the lubricant to be evaluated. A fourth 1⁄2in. diameter steel ball, referred to as the top ball, is pressed with a force of 40 kgf (392 N) into the cavity formed by the three clamped balls for three-point contact. Then the top ball is rotated at 1200 rpm for 60 min.

Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls. The four-ball wear-test method can be used to determine the relative wear-preventing properties of greases under the test conditions

Figure 4(d) depicts the wear scar diameter of various bio-lubricants. The wear scar diameter of bio-lubricants significantly decreases as compared to that of SAE 20W40. The corresponding values are 0.65 mm, 0.58 mm, 0.53 mm and 0.66 mm respectively for TMCO, COME, CMCO and RCO based bio-lubricants, whereas for the lubricant SAE 20W40 is 0.69 mm. The use of Transesterification process for converting RCO into methyl ester increases anti-wear properties. The Polar structure and elongated fatty acid chain composition of methyl ester that gives it the property to stick between mating and moving surfaces, giving it higher wear resistance.



	SAE 20W40	RAW CO	TMCO	COME	CMCO
🟥 Series1	0.69	0.66	0.65	0.58	0.53

Figure 4(d): variation of wear scar, mm for various formulations

4.5.4 Pour point

If oil is cooled, it will start solidifying at some temperature. This temperature is known as cloud point. This cloudiness or haziness of the oil interferes with its flow at low temperatures. The pour point is that temperature just above which the oil sample will not flow under certain prescribed conditions. This temperature is largely determined by the wax content of the oil since as the temperature is reduced was crystallizes out in long needle shaped crystals, forming honeycomb with oil held in the voids between the crystals.

Generally oil derived from paraffinic crudes tends to have higher pour points than those derived from naphthenic crudes. The pour point can, however be lowered by the addition of a pour point depressant usually a polymerized phenol or ester. These substances function by depositing insulating films on the wax crystals as they began to separate out from the oil and by reducing the size of the crystals.

The pour point is that temperature just above which the oil sample will not flow under certain prescribed conditions. It is the most important property of lubricating oil operating at very low temperatures.it tells about the utility of oil at very low temperature applications. The lower the pour point is, the better it is for lube oil.

Figure 4(e) summarizes the pour point of various lubricating oils. This test is carried out as per ASTM d97 test procedure to find out the pour point of oils. SAE 20W40 lubricant offers exceptionally low pour point of -21°C as compared to that lubricants derived from vegetable oils i.e. bio-lubricant. Pour point depressant additive in SAE 20W40 engine oil could be the main cause for extremely lower pour point. The corresponding values were -10°C, -6°C, -9°C & -10°C for TMCO, COME, CMCO and RCO based bio-lubricant respectively. However all the formulated bio-lubricants provide safe working limits during cold climatic conditions. Still the pour point of bio-lubricants could be reduced by adding bio-degradable pour point depressant which was not a part of ingredients in the formulated lubricant.

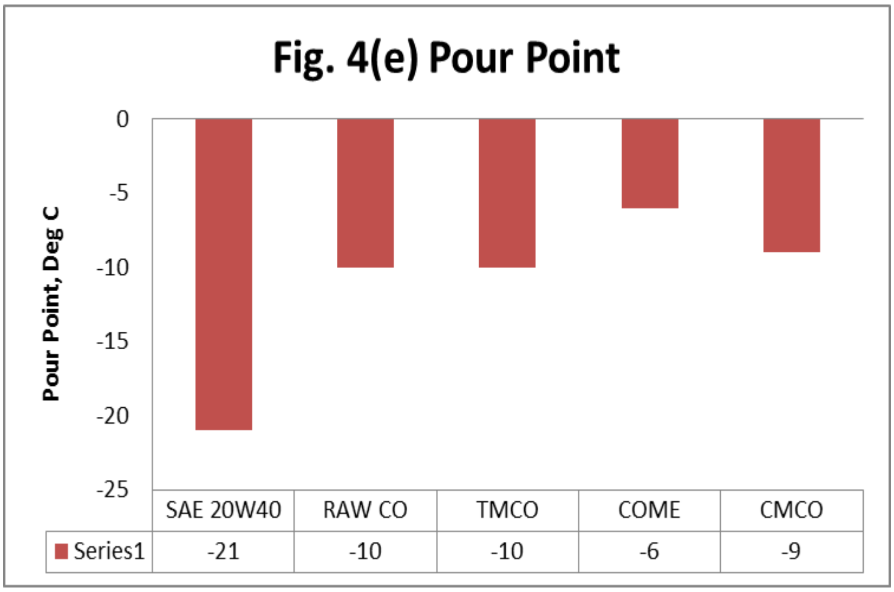


Figure 4(e): variation of pour point , °C for various formulations

4.5.5 ROTARY BOMB OXIDATION TEST

Oxidation stability of oil is its resistance to oxidation. Due to oxidation the oil will form deposits on the piston rings and will lose its lubricating property. The products of oxidation vary widely according to the type of oil and the temperature reached which includes carbon, sludge and organic acids which can be corrosive to certain metals [117]. Thus the oxidation stability of lubricating oils should be as high as possible to reduce the possibility of deposits in the engine.

The most common test to measure the oxidation stability of the oil is the rotating pressure vessel oxidation test (RPVOT) - ASTM D2272, formerly called the rotating bomb oxidation test (RBOT). In essence, the test involves placing a sample of oil into a pressure vessel along with a ration of water and a copper coil. The vessel is pressurized to 90 psi with pure oxygen and placed in a heating bath set at 150°C on a device that rotates at 100 rpm. As the temperature of the pressure vessel and its content increases, the pressure increases. The point at which it stabilizes is defined as T0, which represents the start of the test. Over time, the oil’s ability to resist oxidation degrades as a result of stress-induced additive depletion, to the point where the base oil starts to react with the oxygen as the oil molecules begin to oxidize. Because the oxygen is being incorporated into the oil’s chemistry, the pressure within the sealed pressure vessel begins to drop. The point at which the pressure drops by 25 psi from the pressure at T_0 defines the termination of the test, denoted as T_1. The time, in minutes, required to go from T_0 to T_1, is reported as the oil's RBOT. The RBOT time for CMCO was found to be highest with a time of 49 min while that of TMCO, COME and RCO was found to be 19 min, 32 min and 17 min respectively.

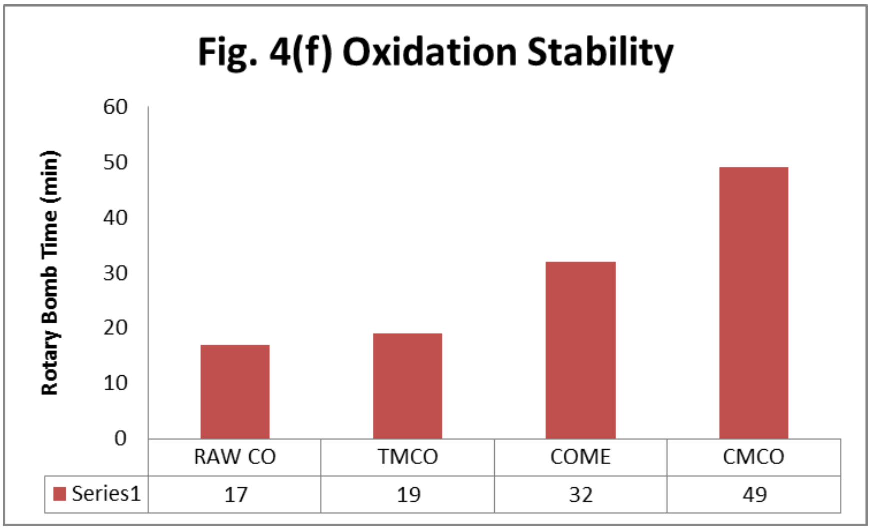


Figure 4(f): variation of rotary bomb time (min) for various formulations

4.5.6 Flash point

The temperature at which the vapour of an oil flash when subjected to necked flame is known as the flash point of the oil. If the container is closed at the time of the test it is called closed flash point, and if open it is called open flash point. Fire point is the temperature at which the oil, if once lit with flame will burn steadily at least for 5 seconds. This is usually 11°C higher than open flash point and varies from 190°C to 290°C for the lubricants used for the internal combustion engines.

Fire and flash point are good indication of relative flammability of the oil and except for the safety for fire hazards; they do not have any significant for engine operation. However, fire and flash point of used lube oil are a very good indication of crank case dilution. The light end of the fuel, which leak in to crank case, readily evaporate and burn at a considerably at a lower temperature than the temperature at which the oil would have burned, clearly indicating the degree of dilution.

The Figure 4(g) shows the flash point of various formulations. The raw castor oil (RCO) showed a flash point of 230°C in comparison to SAE20W40 lubricant which is 200°C .The flash points of TMCO, COME, and CMCO were found to be 220°C, 205°C and 236°C respectively.

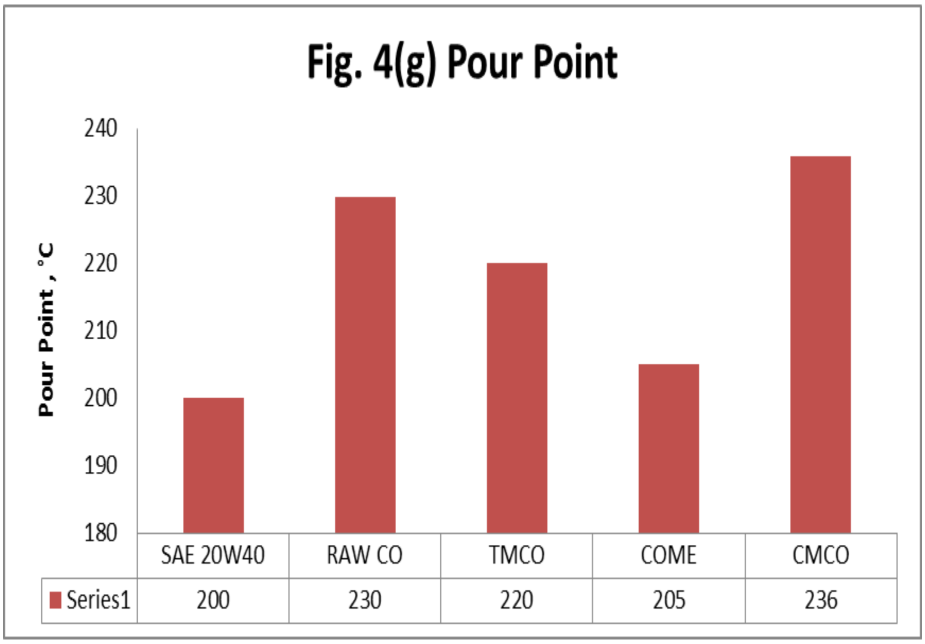


Figure 4(g): variation of flash point of various formulations

CHAPTER 5

CONCLUSION AND FUTURE SCOPE

5.0 CONCLUSIONS

The current experimental research aimed at the validation of castor oil based bio-lubricant formulations for use as conventional lubricant SAE 20W40.

For the above mentioned purpose various formulations of castor oil viz. raw castor oil (RCO), thermally modified castor oil (TMCO), castor oil methyl ester (COME), & chemically modified castor oil (CMCO) were formed.

Finally all the formulated bio-lubricants were subjected to various tribological tests viz. evaporative loss, viscosity index, iodine value, pour point, oxidation stability and four ball wear test. Results were analysed and compared with conventional synthetic lubricant SAE 20W40.

After all the exhaustive research studies and experimental work the following can be concluded:

- Lubricants are complex formulations made up of 90% base oils mixed with 10% additives. The lubricant base oils are mainly mineral oil based. Large order utilisation of lubricants that are being derived from mineral oils are one of the foremost reasons for number of environment issues like surface water pollution and groundwater pollution, Air pollution, soil pollution and food contamination. Mineral oil based lubricants are highly toxic, non-biodegradable and highly hazardous to the environment.
- Another major issue with mineral oil based lubricants is that these are petroleum products. Due to rapid growth throughout the world over the last few decades the petroleum products are depleting at an exponential rate and are bound to extinction in the near future.

- Thus due to the above mentioned reasons, there is a great need to replace base oils of lubricating oils from mineral oil to some renewable and biodegradable oil.
- In the above mentioned regard, vegetable oils as base oils for lubricants appears to be the apt substitute to mineral oil base as they have great properties such as high viscosity index, great lubricity, anti-wear properties and biodegradability.
- However they also possess some drawbacks like poor oxidation stability and pour point. The problems of poor oxidation stability was tried to be resolved by chemical modification of vegetable oil via epoxidation and also through transesterification, which also helped in studying the lubricating properties of esters.
- For the current research work, castor oil was chosen as base oil due to its exceptional lubricating properties as high viscosity index, great lubricity and low pour point.
- The results confirmed that the evaporative loss of castor oil based bio-lubricant formulations were much less than the SAE 20W40 oils. This might be due to the fact that the size of the molecules in vegetable oils are highly consistent. Low evaporative loss leads to lower oil consumption.
- The results clearly showed that the viscosity index of castor oil based formulations is very high as compared to SAE 20W40. The unique structure of vegetable oils having a high order consistency in molecular weight can be the major reason behind this. This unique molecular interface of vegetable oil also leads to oil having high VI. Also the ricinoleic acid present in high amount in castor oil is also one of the reasons for high viscosity index.
- It was proved from the iodine value test results that the chemical modification of the castor oil led to a low iodine value which signifies decrease in the number of unsaturations thus conforming increase in oxidation stability.
- Also it can be concluded that transesterification of castor oil to form castor oil methyl ester led to decrease in iodine value as compared to raw castor oil, thus signifying an increase in oxidation stability.

- Four ball wear test results showed that the anti-wear characteristics of castor oil based formulations are much superior than mineral oil based lubricant.
- It was also found that the pour point of castor oil based formulations was low but SAE 20W40 showed extremely low pour point. But the pour point of castor oil based bio-lubricant is within the safe limits.
- The rotary bomb oxidation test showed that the oxidation stability of castor oil was increased by chemical modification and transesterification. Thus the purpose of chemical modification was successful.
- After all the exhaustive research work it can be suggested that chemically modified castor oil showed all the suggestive properties to be utilised as a bi-lubricant

5.1 FUTURE SCOPE

As part of future research work the formulated bio-lubricants can be subjected to a non-destructive engine test and engine trial of the bio-lubricant can be done to study the friction and wear properties of the bi-lubricant after the engine trial.

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