DEVELOPMENT AND EVALUATION OF MINERAL OIL BASED LUBRICATING OIL BLENDS OF PONGAMIA AND JATROPHA

A thesis submitted to the
University of Petroleum and Energy Studies

For the award of
Doctor of Philosophy
in
Mechanical Engineering

BY

Yashvir Singh

June 2020

Supervisor

Dr. Rajnish Garg

Department of Mechanical Engineering
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Dehradun-248007, Uttarakhand

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DECLARATION

I hereby affirm that my research work entitled **"Development and Evaluation of Mineral oil Based Lubricating oil blends of Pongamia and Jatropha"** for the award of Doctor of Philosophy from University of Petroleum and Energy Studies, Dehradun is my own original work and has not been submitted for any assessment or degree/diploma or award at the University of Petroleum and Energy Studies or any other University/Institutions.

Yashvir Singh

SAP ID: 500024452

Date: 8-6-2020

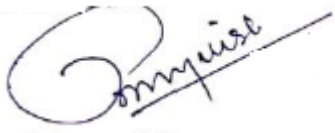
UPES
UNIVERSITY WITH A PURPOSE

CERTIFICATE FROM SUPERVISOR

This is to certify that the thesis on **"DEVELOPMENT AND EVALUATION OF MINERAL OIL BASED LUBRICATING OIL BLENDS OF PONGAMIA AND JATROPHA"** by **YASHVIR SINGH (SAP ID-500024452)** in partial completion of the requirements for the award of the degree of Degree of Philosophy is an original work carried out by him under my supervision and guidance.

It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University.

Internal Guide



Dr. Rajnish Garg

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Date: 8-6-2020

Place: Dehradun

ABSTRACT

Based on the environmental concerns related to the pollution caused by the vehicles and the demand for an alternative to the conventional lubricant resulted in the studies to be conducted which are environmental-friendly. To cope with the situations, non-edible oils are an alternative resources available. The pongamia and jatropha oils are the substantial candidate available for the tribological applications. They are available in abundant amount in several parts of the world including India, Malaysia, South Korea, China, Africa etc. The quantity of the seeds obtained from these type of feedstocks are in abundant amount and are capable to produce oil ranging between 25% to 57% based on the atmospheric conditions. In this study, tribological characterization was performed to examine the potential of mineral oil based blends of pongamia and jatropha and to observe their tendency for the application as an alternate lubricant to the conventional oil. Before the test was conducted, the crude oil of both the feedstocks was chemically modified using two step transesterification process with further chemical reaction with trimethylolpropane. They are blended with the mineral oil in certain proportions consisting of 5%, 10% and 15% blends (% by volume). The pin on disc tribometer was considered for the tribological analysis under various operating conditions including normal load ranging from 40 to 200 N, sliding speed 300 to 1500 rpm and sliding distance of 30000 m. The temperature was maintained constant by using the insulated heating element equipped with the pin-on-disk machine. For the examination of the wear scar diameter, view 7 software equipped with the optical microscope was used. For the worn surface characterization, SEM was used consisting of

high resolution capacity. Based on the study performed, 5 and 10% concentration of the modified pongamia and jatropha oil showed an improved results by reducing COF, wear rate, mean wear scar diameter and improved the worn surface morphology with comparison to the mineral oil. The maximum increment in the response parameters was obtained with relative to their tribological analysis when the concentration of the modified pongamia oil increases beyond 10% and reaches 15%. The variation in the operating parameters play a significant role during the tribological analysis of the surface in contact. Maximum influence was obtained at higher load and minimum sliding speed. Maximum distortion of the material was obtained at conditions consisting of maximum load, minimum speed and higher amount of lubricant blend ratio of 15%. With an increase in sliding speed, reduction in the friction coefficient was observed at minimum load due to increase in the proportion of the hydrodynamic lubrication.

With respect to the comparison of modified pongamaia and jatropha oil, jatropha oil shows better results with reference to all the conditions applied. The amount oleic acid is more in jatropha oil in comparison to the pongamia oil which helps in sustaining an improved protective layer during surface interaction. Conclusively, the performance of 5% and 10% blend samples are having better potential impact during the tribological analysis as a lubricant with respect to the environmental concern and energy saving. To correlate the parameters of the POD tribometer and the diesel engine, response surface methodology technique has been applied. The model developed is quite significant and useful for the determination of the wear at the considered

operating conditions. This indicates that the parameters like load, sliding speed, and lubricant blends are the acute parameters in respect of the alteration of the tribometer test runs to real engine conditions.

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Finally, but by no means least, I am thankful to my parents and wife for almost unbelievable support. They are the most important people in my world and I would like dedicate this thesis to them.

LIST OF SYMBOLS

a	Radius of circular region	m
A'	Cross sectional area of ploughing track	m^2
A_r	Real contact area	m^2
d	Track width of wear scar	m
F	Friction force	N
F_s	Shearing force	N
F_p	Ploughing force	N
H	Indentation hardness	N/m^2
k	Thermal conductivity	W/mK
K	Thermal diffusivity	m^2/s
K	Wear coefficient	-
L	Wear scar length	m
l_b	Effective diffusion length	m
N	Normal load	N
p, P	Contact pressure	N/m^2
P_e	Peclet number	-
Q	volume removed per unit sliding distance	m^3/m
q	Heat generated per unit area	W/m^2
R	Radius of curvature	m
r	Ball radius	m
S	Shearing strength	N/m^2
SWR	Specific wear rate	mm^3/Nm
TAN	Total acid number	mgKOH/gm
Tb	Total contact temperature	^oC
Tc	Bulk material temperature	^oC
$Tnom$	Nominal contact temperature	^oC
Tf	Flash temperature rise	^oC
U	Dimensionless speed	-

V	Velocity	m/s
V_w	Total wear volume	m^3
w	Wear scar width	m
W	Dimensionless load	-
WSD	Wear scar diameter	mm
μ	Coefficient of friction	-
ρ	Density	kg/m^3

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
COF	Coefficient of friction
JB	Jatropha oil blend
PB	Pongamia oil blend
M	Mineral oil
POD	Pin on disc
RSM	Response surface methodology
SAE	Society of automotive engineers
SEM	Scanning electron microscope
ZDDP	Zinc dialkyl dithiophosphate

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CHAPTER 1

INTRODUCTION

1.1. Motivation behind the research work

Among the population of the World, India comes out to be the second-largest country consisting of around 1.32 billion population (according to the 2018 estimate). To fulfill the country's energy demand is one of the most difficult tasks. The government and the policy makers face certain challenges while defining policies related to the energy sector. In recent years, the Indian government has taken several steps to secure the energy available and now focussing on the renewable energy resources available due to the environmental deterioration problems in the country [1, 2].

Several studies have been conducted to analyse the renewable energy resources available in the country. Due to the increased demand for energy in different sectors and the import of crude oil from various countries enforced the Government to take some relevant measures while considering alternative approaches. Several policies have been implemented so that the increased demand for energy can be fulfilled while implementing renewable sources. But the development of the country and the future demand for energy needs a rigorous exercise that needs further analysis. This study has been conducted to fulfill some of the gaps remaining while developing alternate energy sources [3-5].

The country per capita energy consumption is 3.78 times minimum than the world average energy consumption based on the year 2010, but the growth is 2.48 times higher. The higher growth rate contributes at consuming more energy rates as compared to the global energy consumption rate. India is the third-largest energy-consuming country after China and USA, with a global share contribution of 5.6%. Hence, it is very much expected that the energy requirements of India are supposed to increase in the upcoming years to meet the global average energy consumption level.

There is a substantial energy requirement of India to meet the energy demands in the upcoming years and to maintain a progressive economic growth

rate. While distributing and supplying energy to the different sectors, environmental deterioration are of great concern. The country sectors are highly dependent on resources like fossil fuels which are depleting at a faster rate [6].

The total primary energy requirement of India is met by the different energy sources consisting of coal, crude oil, and other renewable resources. Around 43.2% energy requirement are met through coal, 24.1% by crude oil, 23.7% by renewable sources and the rest by other available resources. During the last decade, the increased demand of the energy has been fulfilled by setting up more thermal power plants in which coal, natural gas and oil are the prime suppliers of the energy. Without any considerable intensification in the production of domestic crude oil over the years and the deficiency of divergence of energy sources integrated with faster economic growth rate results in the import of crude oil. The dependence of the country on a large scale on non-renewable resources creates threats to the environment which required major concentration towards the availability of renewable resources [7-9].

In transportation sector, the lubricant is required to minimize the friction and wear of the surfaces during their sliding contact during application in engines. The petroleum-based product, mineral oil plays a considerable role as lubricant required during the lubrication process. Friction is the process that develops when the surfaces are in contact during the motion. This results in the production of heat leading to the increment in the temperature. In the automotive sector, friction is desired in certain parts of the vehicle including braking system, belts and clutches. However, in several situations like piston ring interface friction results in the decrease in mechanical efficiency and increase in the specific fuel consumption. Increment in the friction produces heat resulting in the seizure of the piston movement in the engine [10].

Wear is associated with the interaction of the contact materials during the rolling process and caused by the surfaces rubbing against each other. Automotive components have to be substituted with the new one if minor wear occurs on the surface. Excessive wear result in the decrement of the life of the equipment's.

Lubrication is the process with the help of which friction and wear can be reduced by applying lubricant to the surfaces in contact. The functions are (i) to produce a protective lubricant film between the metals during their contact (ii) reduce the heat produced (iii) removal of metal debris from the oil.

In *hydrodynamic lubrication* very thick fluid film is formed between the surfaces in contact which is more than the height of the roughness available on the bearing surfaces [11]. During this lubrication process, the proper lubricant is supplied between the surfaces during their contact. The hydrostatic pressure generated in the film does not lead to any distortion of the surfaces during their proper contact. In *Elastohydrodynamic lubrication*, the local pressure generated is higher and creates a significant distortion of the surfaces during their contact. In *boundary lubrication*, the surfaces are separated due to the formation of the molecular film created by the adsorbed oil or grease on the surfaces of the metal in conatcts [12-16]. The lubricant maintained a layer between the piston ring interfaces to provide an optimum engine performance and wear protection. The proper design of the lubrication system is desired to increase the engine life and proper working of the system [17-19].

The most of the lubricants are originated from the mineral oil and consists of various hydrocarbon chains with molecular weights varied between 300 and 600. Fig 1.1 shows the molecular structure related to the conventional lubricant. The major part of the molecules contained saturated long-chain hydrocarbons involving straight or branched chains with 15–30 carbon atoms. The naphthenes hydrocarbon rings contain 5 or 6 membered saturated rings with attached side chains consisting of 20 carbon atoms [20]. A small amount of aromatic components are also present containing one or more benzene rings with saturated sidechains. Some other components may be present in reduced amounts [21-23].

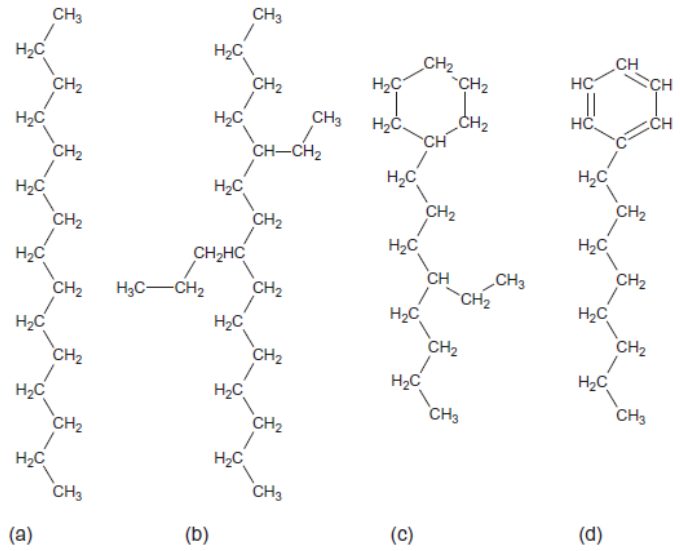


Figure 1.1. Hydrocarbon molecules present in mineral oil: (a) paraffin; (b) branched paraffin; (c) naphthenic; (d) aromatic.

The increased commercialization of the industries and improved living standards exponentially increased the demand for the energy [24]. Fig. 1.2 shows the world energy consumption status which has significantly increased within recent years [25]. The increased energy demand directly influences the requirement of fossil fuel products. A further amounts of petroleum products including fuel and lubricant are required to compensate for the increased energy demand. The annual consumption of the lubricant varied between 32 to 45 million tons in which 25 million tons of the lubricant returned to the environment resulting from its degradation as they are harmful to the environment. The prime focus is needed at this point as petroleum-based lubricants are non-renewable and highly toxic. The combustion in engines and inappropriate disposal of these lubricants are harmful to the environment due to their higher toxicity and non-biodegradability [26-28].

The discard of the used mineral oils is one of the major factors responsible for environmental pollution which needs to be addressed. Due to human negligence, oil spillage to the land, particularly to the aquatic environment are considerable concerns [29]. The spillage of the oils into the sea is based on the offshore oil boards and trading of oil tankers.

The discard of the oil to the environment was around 34,000 tonnes in volume between 2010 and 2016. Table 1.1 shows the oil spillage cases that

happened during these years [30]. The spillage of the oil is harmful to the aquatic environment and the survival of the plant and animals is difficult because the layer of oil gets form on the liquid surface which prevents the approach of sunlight to the aquatic environment [31].

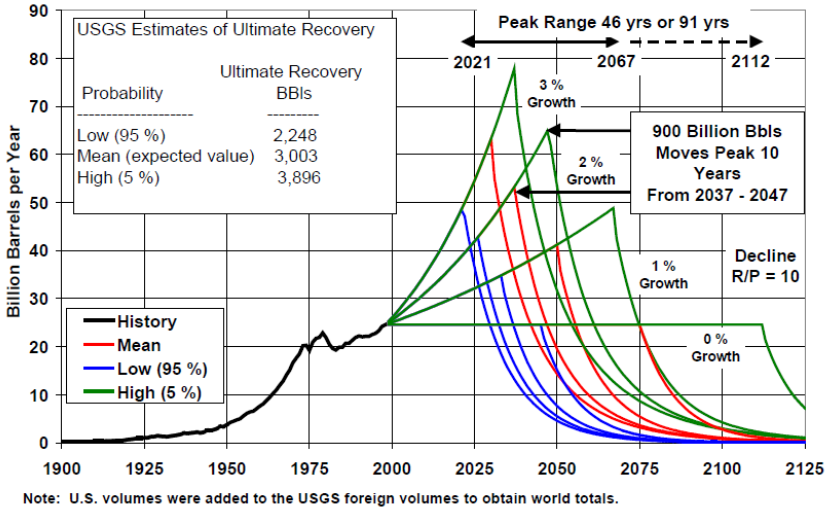


Figure 1.2. The world oil production estimates [25].

Table 1.1.

The annual oil spillage between 2010 and 2016 [30].

Year	**7-700 tonnes**	**> 700 tonnes**
2010	5	4
2011	4	1
2012	7	0
2013	5	3
2014	4	1
2015	6	2
2016	4	1
Total	35	12
Average	5	1.7

The faster depletion of the petroleum reserves and the increased pollution level of the environment have raised several concerns [32-34]. Various steps are considered in this direction to minimize harmful environmental hazards. The development of an alternative to the petroleum-

based mineral oil is one of them. The sustainability of the bio-based lubricant or bio-lubricant derived from bio-based resources like vegetable oils is one of the options available. The bio-based lubricant derived from the vegetable oils are having higher lubricity, higher viscosity index, higher flash point, and good anti-wear properties with concerning conventional lubricant. Despite several advantages of non-edible oils, certain challenges are there which need to be addressed before their commercial usage. Such efforts can promote the usage of bio-lubricants in the transportation sector and also contribute in handling the environmental issues [35].

1.2. Problem statement

Vegetable oil-based lubricants can become a better alternatives to the available lubricant base stocks. Many studies were conducted and stated that genetically and chemically upgraded vegetable oils have a good opportunity to act as an alternate lubricant for the automotive sector [35]. In earlier days, vegetable oil has already been used as a lubricant for automotive and machinery applications for a long duration before the development of petroleum-based products. The petroleum-based mineral oil is generally cheaper and provides better lubricity to the engine components with comparison to the vegetable oil-based lubricants [36]. With an increase in petroleum product costs due to international requirements and political factors, diminishing petroleum natural reserves, and environment pollution are the important points which needs to be addressed while implementing an alternate approach. The vegetable oil-based lubricant applications are slowly developing and will constantly comeback in the upcoming future [20, 37].

For the improvement of the vegetable oil-based lubricant physicochemical properties, several studies were conducted so that the dependence on conventional lubricants can be reduced [38, 39]. The presence of a polar group in vegetable oils consisting of a long hydrocarbon chain could result in the improvement in the properties of the vegetable oil which acts as amphiphilic surfactant adsorbed on the surface of the metals and results in the formation of the improved lubricant film. The polarity of the vegetable oils is one of the prominent factors which could minimize friction and wear of the surfaces while forming a better protective film between the surfaces [40].

Various methods are considered to modify the properties of the vegetable oils in which chemical modification is one of them. The chemical modification routes are one of the ways with the help of which vegetable oils become capable to withstand different operating conditions with the help of forming a protective layer between the surfaces. [41, 42].

Most of the studies aforesaid are related to the tribological analysis of the edible vegetable oils. In addition, the temperature considered during the tribological characterization was considered below 100^{o}C which is not sufficient to study the degradation of the lubricant during its application in engines. Furthermore, the development of the model to correlate the operating parameters of the tribometer to the real engine parameters have not been discussed earlier.

The tribometer can be considered to analyse the accurate tribological behaviour of the bio-based vegetable oils. The motion between the piston rings and the cylinder liner is one of the crucial factors to be considered while the analysis of vegetable oil-based lubricants with variation in the applied load. The implementation of the different loads, sliding speed and sufficient temperature are needed to be considered in a very precise way during the characterization of the tribological analysis.

1.3. Purpose, objectives and research scope

1.3.1. Purpose

The purpose of this study is to analyse the tribological behaviour of the modified non-edible oils at different operating conditions and to correlate the parameters considered during the analysis on tribometer with the real engine conditions.

1.3.2. Objectives

To achieve this aim, the following objectives are identified:

a) Physical characterization of jatropha oil and pongamia oil based bio-lubricant blends.
b) Investigations on friction and wear characteristics of jatropha oil and pongamia oil based bio-lubricant blends at different set of operating parameters and selection of best bio-lubricant blends.

c) To correlate the experimental conditions like load, sliding speed etc. with the real operating conditions in a diesel engine.

1.3.3. Research scope

The following research scopes are identified.

a) The non-edible oils utilized were restricted to the pongamia and jatropha oil only.
b) The pin-on-disc tribometer was utilized to examine the tribological characteristics.
c) The test parameters were varied at various test conditions including the changes in load, speed and lubricant ratio.
d) Parameters selected on pin on disc tribometer were correlated to the real diesel engine.

1.4. Outline of the thesis

The present study includes six chapters which are stated in this section for the purpose to outline the work performed during this investigation.

Chapter 1 includes the motivation section describing the basic idea before conducting this study. It also includes the research gap which has been identified to address the issues which have not been analysed before. The futher section includes the purpose, research scope and objectives defined during this study. The novelty and the significance of this study have also been stated at the end of this chapter.

Chapter 2 mentioned the literature survey related to the previous work stated so far. During the starting phase, the introduction of the bio-based lubricants are described in a detail. After this, the resources, advantages and processes implemented for the production of the bio-based lubricant are described. The benefits of using non-edible oils as bio-based lubricant are discussed in a descriptive way while considering their benefits, applications, and the feedstocks available around the world. Further, the tribological study conducted while considering the non-edible oils as alternate and the parameters considered during their study is mentioned. Also, lubricant market demand is also stated at the end of this chapter.

Chapter 3 described the materials and methods considered before the tribological analysis of the non-edible oils. This chapter described the details of

the chemical process considered for the improvement in the properties of the non-edible oils. The equipment and engine test rig details are mentioned are in detail to investigate the tribological characterization of the modified oils and their surface analysis.

Chapter 4 includes the result and discussion section. In this chapter, the triboloical analysis was done while considering the different conditions including variation in sliding speed and load. The comparison between the different non-edible oils is also stated with further justification while considering the previous work conducted. The details about the measurement methods for the wear scar diameter analysis are also declared in order to get a detailed analysis of the surfaces considered during this study. At the last stage, the model is developed to correlate the parameters involved in tribological analysis with tribometer to the real engine parameters.

Chapter 5 summarized the finding observed during this study. The finding achieved are properly correlated with the objectives considered during this investigation. Future work is also suggested in this section which can be considered for better improvement of the properties of the non-edible oils. At the end of the sub-sections, the work published based on this study are also presented.

Chapter 6 includes the references taken during the present study.

1.5. Significance and novelties of the study

Futher sections described the details about the significance and novelty involved in this study.

1.5.1. Significance

a) Only a few studies have been performed related to the tribological analysis of non-edible vegetable oils and the use of pongamia, jatropha oil for the assessment of the tribological applications has not been aforesaid in the literature.
b) Very few investigations are there on the comparison of bio-lubricant lubricity with the conventional lubricant. Most of the researches has been conducted with comparison to diesel fuel as reference.
c) Very few studies have been performed on the development of the model with the utilization of the conventional lubricant in the engine. The

development of the model with the use of bio-lubricant has not been addressed in the literature.

d) Correlation of the parameters associated with the engine performance during the test on the reciprocating test bench has not been addressed in the literature.

1.5.2. Novelty

In view of the aforementioned issues, the present work was aimed at the utilization of the pongamia and jatropha oils for the tribological applications. Bio-lubricant has been developed and the tribological study was performed at different load and sliding speed. Further, optimization of the operating conditions has been performed using response surface methodology.

The Novelty elements in this research work are (i) Utilization of the bio-lubricant blends for the tribological analysis and their comparison with the mineral oil, (ii) Development of the model including important operating parameters, (iii) Selection of the best suitable bio-lubricant blends and correlation of the parameters with the diesel engine parameters.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

Many researchers around the globe have attempted to improve environmental friendliness, dependability, and energy efficiency of the automotive sector. Advancement in technological solutions like the use of lightweight materials, exhaust gas after treatment, less harmful fuel, and controlled combustion are a few means that have been suggested as ways to decrease the environmental problems created by vehicles and machines [43].

Lubrication is the process, or technique employed to reduce wear of one or both surfaces in close proximity, and moving relative to each another, by interposing a substance called lubricant between the surfaces to carry or to help carry the load (pressure generated) between the opposing surfaces. The main purposes of lubrication are (i) to reduce wear and prevent heat loss that results due to contact of surfaces in motion, (ii) to protect it from corrosion and reduce oxidation; (iii) to act as an insulator in transformer applications; and (iv) to act as a sealing agent against dirt, dust, and water. While wear and heat cannot be completely eliminated, they can be reduced to negligible or acceptable levels by the use of lubricants. As heat and wear are associated with friction, both effects can be minimized by reducing the coefficient of friction between the contacting surfaces. Any material used to reduce friction in this way is a lubricant. Lubricants are available in liquid, solid, and gaseous forms, amongst which liquid and solid or semisolid are used widely in day to day life [35, 44].

The requirement of effective lubrication at desired operating conditions for safe and reliable operation of an automotive vehicle is mandatory to reduce friction and wear, particularly in engines and drivetrains. For a long time, mineral oil has been used as a lubricant for automotive applications. But, being a distillation product of crude oil, its use is limited by the availability of crude oil reserves. In addition, the disposal of mineral oil leads to the degradation of both aquatic and terrestrial ecosystems [45]. Furthermore, emissions of metal traces like calcium, magnesium, iron particles, and zinc due to the combustion

of mineral oil as a lubricant lead to concerns about environmental degradation [46]. Moreover, current and future prospects of mineral oil as a lubricant in automobile engines have been predicted as bleak for the future [47]. Hence, there is a need to identify a suitable alternative to mineral oils in internal combustion engines.

In the transportation and industrial sectors, the world relies heavily on petroleum-based products which may cause grave concern related to future energy security. In certain cases, these products would end up back to the environment causing serious environmental pollution and hazards. Recognized as potential substitutes for mineral-based lubricants, bio-based lubricants have received growing interest as they play a significant role in overcoming problems mentioned. Bio-based lubricants have been found to exhibit superior lubricant properties over the conventional mineral lubricants, with renewability and biodegradability being their strongest suit [48]. The depletion of crude oil reserves and an increased hike in oil prices have led to an innovative global search for developing and using alternative lubricants to protect the environmental deterioration caused by the lubricating oils and their uncontrolled spillage [49]. Bio-lubricants can be considered as an alternative to mineral oils due to their natural technical properties and biodegradability [50]. The presence of long-chain fatty acid and polar groups in the structure of vegetable oils make them suitable for both boundary and hydrodynamic lubrication [51, 52]. There are various sustainable feedstocks for the production of bio-lubricants. There are limitations on the suitability of edible vegetable oil feedstock due to the latest concerns about their involvement in the human food cycle and environmental degradation caused by the use of available cultivation land. The involvement of edible vegetable oil feedstock could cause ecological imbalances due to the cutting down of forest land for plantation purposes [53, 54]. Therefore, non-edible plant oils are prominent for application as bio-lubricants in the diesel engine industry [55].

Around the world, 350 oil-bearing crops are available [56]. The use of non-edible oils can be guaranteed as a sustainable feedstock for bio-lubricant since most of the non-edible plants can be grown on wastelands to reclaim them, not compete with food crops for limited lands, are relatively cheap, available

and offer similar or even higher yields of bio-lubricant and fuel properties as the edibles [57]. Crops bearing non-edible vegetable oil seeds are jatropha curcas, polanga, karanja, neem, mahua, castor, jojoba, coriander, hingan, mongongo [58].

Other non-edible oils such as n*icotiana tabacum* (tobacco), *acrocomia aculeate* (macaúba), *crambeabyssinica* (hochst), linseed oil, rubber seed oil, s*apium sebiferum* (chinese tallow), s*apindus mukorossi* (soapnut), *euphorbia tirucalli* (milk bush), c*alophyllum inophyllum* (polanga) and nahor oil have been used as feedstock [59]. Therefore, more emphasis is now given to non-edible seed oils as a source of bio-lubricant. A lot of researchers have reported the use of non-edible vegetable oil as an engine fuel but only a few have reported the use of non-edible vegetable-based lubricants for automotive applications [54, 60, 61].

The main aim of this present study is to provide information to the researchers, policy makers, industrialists and engineers who are involved in the use of bio-lubricants. It presents a detailed review of the prospects of using non-edible vegetable oil-based bio-lubricants as alternative lubricants in the automotive sector. This study includes the various research papers published in highly rated journals including the recent studies conducted.

2.2. Methods

This section explains the systematic methodology used in the search of the literature. A three-stage analysis framework is implemented. In the first part of the review process, namely the "identification" process, various publicly available sources have been chosen for the literature search e.g. www. siencedirect.com. www.scopus.com, etc.

Keywords used for literature search are listed in the search strategy Table 2.1. Research papers that involve bio-based lubricants, their physicochemical properties, and tribological performances were given the priority during selection without any restrictions. The type of publication considered for this work includes articles, book chapters, and international books.

The second stage is the "screening" process. For the initial screening process, all duplicate publications resulted from multiple database searches are

identified and removed. Then, the abstract of the remaining publications is checked before being sorted according to sections. From this process, it is found that most articles were focusing on the properties and the production technology of bio-based lubricants, without reviewing the significance of these properties for the real-life application. Therefore, to fill that gap, this review has been organized into three main sections which are physicochemical properties of different bio-based lubricant categories, tribological behavior of bio-based lubricants and applications of bio-based lubricant.

The third stage is where the eligibility or selection of literature is made. All the relevant works are listed and gathered for further in-depth analysis. A list of inclusion criteria has been established to aid the publication selection process. Table 2.1.

Strategy table

Keywords searched	• "Bio-based lubricant, bio-lubricant, non-edible vegetable oil, tribological characteristics, oxidation and degradation are the keywords used for finding research articles.
Databases searched	Databases of following publishers are used: *Sciencedirect, Springer, RSC, Emerald, Wiley, Hindawi* Multiple databases search tool are used for eg. *Scopus, Web of Science, Google Scholar*
Year of Search	No time restriction is there in searching databases
Language	Articles published in English are studied
Inclusion criteria for the studies used	• Studies related to bio-based lubricant development • Studies related to the tribological behavior of bio-based lubricants

	• Study testing the feasibility of bio-based lubricant for various applications. • Study related to the market of the lubricants available and companies involved.
Exclusion criteria for the studies	• Publications which only focused on production methods using chemical modification technique. • Publications of which the results seem to be superficial i.e. investigation of tribological characteristics without comparing the result of bio-based lubricant with the conventional lubricant.

2.3. Friction

Friction is a resistance force to tangential motion between two surfaces in contact. It has been stated that the friction force is proportional to the normal load applied and independent of the apparent area of contact [62]. The friction force, F can be stated by the basic equation:

$$\mu = F/N \quad (2.1)$$

Where, μ is called the coefficient of friction (COF), F is the frictional force, and N is the normal load.

Thereafter, Bowden and Tabor developed a more detailed model of metallic friction. They described the friction force as a summation of two components; the adhesive force, F_s and ploughing force, F_p in which [63]:

$$F = F_s + F_p \quad (2.2)$$

During the relative motion of two contacting bodies, the adhesion force is required to shear the contacting junctions where the adhesion occurs, while the ploughing force is needed to plough the asperities of the harder surface through the softer surface. Bowden and Tabor suggested that the contact occurred only at the surface asperities. This contact area is known as the real

contact area, which is very small, and independent of the apparent area of contact. This real contact area is also proportional to the applied load where the asperities could deform. These come to a formula stating that:

$$F = Ar\,.\,S + A'p \qquad (2.3)$$

Where, A_r is the real contact area, S is the shearing strength of metallic junctions, A' is the cross sectional area of the ploughing track and p is the pressure to cause plastic flow of the softer metal. When the load is applied, the asperities of the softer material deform at the contact region until the real area of contact is sufficient enough to support the load. In this situation $N=p*A_r$. Equation 2.4 then can be written as:

$$F = \frac{Ns}{p} + A'p \qquad (2.4)$$

Finally, the coefficient of friction is given by:

$$\mu = \frac{F}{N} + \frac{S}{p} + \frac{A'p}{N} \qquad (2.5)$$

Bowden and Tabor showed that the ploughing force for ball-on-flat contact is also dependent on the ploughing track width, d and radius of curvature, R of the contact and can be derived as:

$$F_p = \frac{d^3 p}{12R} \qquad (2.6)$$

and this theoretical result agreed with test data (Figure 2.1).

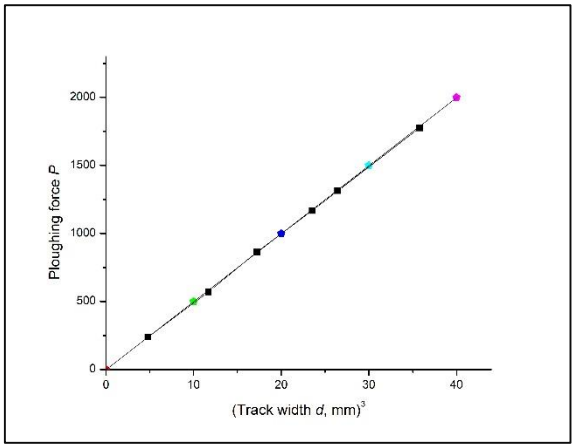


Figure 2.1. Effect of track width on the ploughing force of indium with a flat steel for dry and lubricated surfaces [62].

2.3.1. Tribometer and friction force measurement

Prior to performing tribological research, it is very important for a researcher to understand the system of a test rig or tribometer. Most of the tribometers used for experimental work in tribology are commercially available and designed on a small scale in order to replicate the application in the real system. They include four-ball-tribometers, pin-on-disk-tribometers and linear reciprocating friction testers. A close application for the four-ball-tribotester could be a ball bearing system while the pin-on-disk could duplicate the disc brake system. A sliding motion in a linear reciprocating friction tester could replicate the piston ring motion in an internal combustion engine. Typical configurations of commercial tribometers with the direction of normal load applied are shown in Figure 2.2.

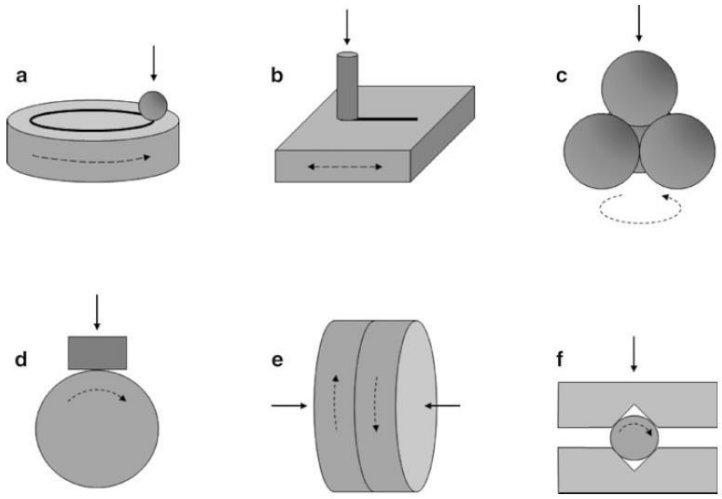


Figure 2.2. Typical configuration of commercial tribometer where normal load is indicated by arrows; (a) ball-on-disc, (b) reciprocating pin-on-flat, (c) four-ball, (d) block-on-wheel, (f) flat-on-flat and (f) pin and vee-block [64].

The basic set-up in friction force measurement for a tribometer is by applying a normal load between two contacting bodies that have a relative motion (one body is moving while the other partner is static). The normal force should be adjustable so that it could be increased gradually until a measurable tangential force is detected by a force measurement device. For evaluating the friction force, F in the linear reciprocating test rig, a spring balance is sometimes used in order the produce an adjustable normal load, N that applied to the

contacting bodies. A calibrated load cell is normally attached to the static body as a friction force measurement device. The coefficient of friction is then calculated by dividing the friction force, *F* by the value of normal load, *N*.

2.3.2. Friction during running-in condition

Running-in is a process of changes in friction and/or wear in tribosystem prior to steady-state when two contacting surfaces are in contact under a normal load and relative motion. The running-in process is an effective way of matching two contacting components and gives important clues to system designers for the identification of various contributions to the overall friction performance of machines. In order to achieve long-term service life, some machines (for example a new engine) are exposed to the certain running-in procedure after assembly. There are eight common shapes of running-in behaviour (friction-time curves) in metal sliding contact that was categorised by Blau [65] based on his literature survey of the tribology tests.

Table 2.2 indicates some of the possible causes for each type of curve. From the outcome of his research, Blau [66] concluded that there was no evidence that these eight curves were representative of specific contact conditions.

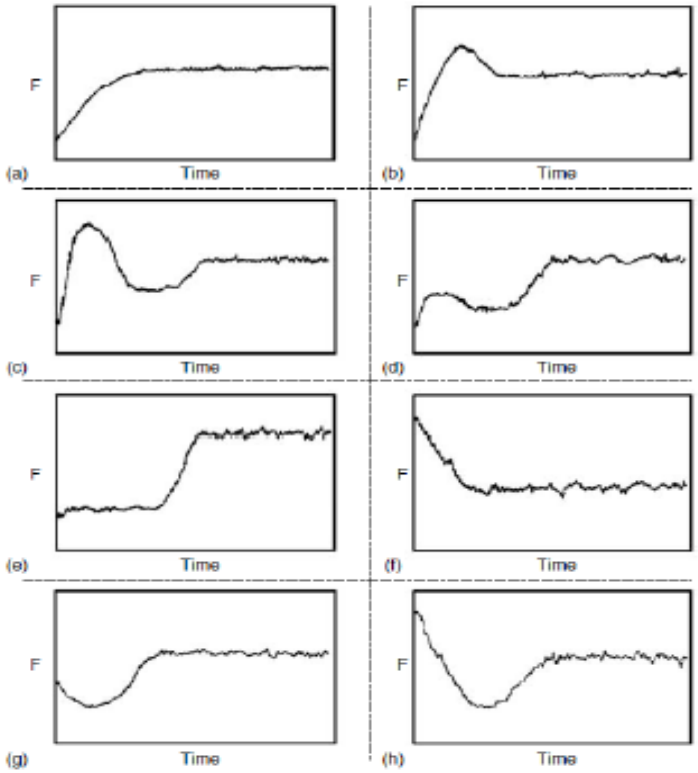


Figure 2.3. Initial friction behaviour during running-in time.

Table 2.2.

Possible causes of friction running-in behaviour as shown in Figure 2.3.

S. No.	**Occurrence**	**Causes**
1	Contaminant surfaces	(i) A thin film of lubricious contaminant is worn off the sliding surface [67]. (ii) Effects of component temperature rises due to sliding friction [68]. (iii) Mechanical disruption of surface oxide films with increasing metallic contact [51]. (iv) Contact geometry changes [62].
2	Boundary-lubricated metals	Surfaces wear-in; initial wear rate high until the sharpest asperities are worn off and surface becomes smoother [69].

3	Unlubricated oxidised metals, often observed in ferrous or ferrous/nonferrous pairs	Wear-in, as in type (b), but with the subsequent development of a debris layer (debris accumulation) or excessive transfer of material [69].
4	Same as type (3)	Similar to type (3), but the initial oxide film maybe more tenacious and protective [69].
5	Coated systems; also, systems in which wear is controlled by subsurface fatigue processes.	Wear-through of a coating; or subsurface fatigue cracks grow until debris is first produced. The debris then creates third bodies, which induce a rapid transition in friction. Sometimes a few initial spikes in friction signal the onset of this transition [70].
6	Clean, pure metals	Crystallographic reorientation of regions in near surface layers reduces their shear strength and lowers their friction. Alternatively, the initial roughness of the surface is worn off, leaving smoother surfaces [71].
7	Graphite on graphite; metal on graphite.	Creation of a thin film during running-in; debris or transfer produces a subsequent rise in friction [72].
8	Hard coatings on ceramics	Roughness changes, then a fine-grained debris layer forms [65].

2.3.3. Frictional heating and contact temperature rise

Part of the mechanical energy used to slide material in frictional contacts dissipates as heat energy. This energy dissipation is known as frictional heating which may contribute to an increase in the temperature of the two sliding bodies. Frictional heating and temperature rise in sliding contacts could affect the tribological behaviour and failure of the sliding components. An increase in surface temperature sometimes is sufficient to cause the melting of material, surface oxidation and possible changes of the structure and material properties

at the contacting areas [73]. The surface temperature on the sliding bodies could be measured experimentally or estimated by calculation. The total contact temperature (T_c) at a given point can be estimated based on the summation of three components:

$$T_c = T_b + \Delta T_{nom} + \Delta T_f \quad (2.7)$$

Where, T_b is the bulk material temperature, ΔT_{nom} is the nominal (or mean) contact temperature and ΔT_f is the short duration flash temperature rise at the various asperity contact.

In the case of a stationary heat source on moving body (with circular region of radius, a), the maximum flash temperature rise can be approximated as [74]:

$$\Delta T f_{max} = \frac{2qa}{k\sqrt{\pi(1.273+P_e}} \quad (2.8)$$

Where, $q = \mu PU$ is the rate of heat generated per unit area (W/m^2), μ is the coefficient of friction, P is the contact pressure (N/m^2), a is the radius of circular region (m), k is the thermal conductivity (W/mK), P_e is the Peclet number = $Va/2K$, V is the velocity (m/s) and $K = k/\rho c$ is the thermal diffusivity (m^2/s).

The nominal surface temperature rise is an additional surface temperature due to a heat source that passes repeatedly over the same point on the surface. The nominal surface temperature rise for the moving body is determined by:

$$\Delta T_{nom} = q_{nom} \frac{l_b}{k} \quad (2.9)$$

Where, $q_{nom} = q \frac{A_r}{A}$, A_r is the real contact area (m^2), $A = \pi a^2$ is the nominal contact area (m^2), $l_b = \frac{a}{\pi^{1/2}} tan^{-1}[\frac{2\pi k}{aV}]^{1/2}$ is the effective diffusion length (m).

2.4. Wear

Wear can be defined as progressive loss of substance from the operating surface of a body occurring as a result of relative motion at the surface [75]. The basic mathematical model of the relationship between wear rate and normal load is given by the formula (Archard wear equation):

$$Q = \frac{KN}{H} \qquad (2.10)$$

Where, Q is the volume removed from the surface per unit sliding distance (m3/m), N is the normal load applied to the surface (N) and H is the indentation hardness of the wearing surface (N/m2) and K = wear coefficient. Archard equation is limited to a linear relationship between the normal load, sliding distance, material hardness and wear volume provided that the K, N and H remains constant during wear test, the volume of material lost from the surface is directly proportional to the relative sliding distance or experiment time [76].

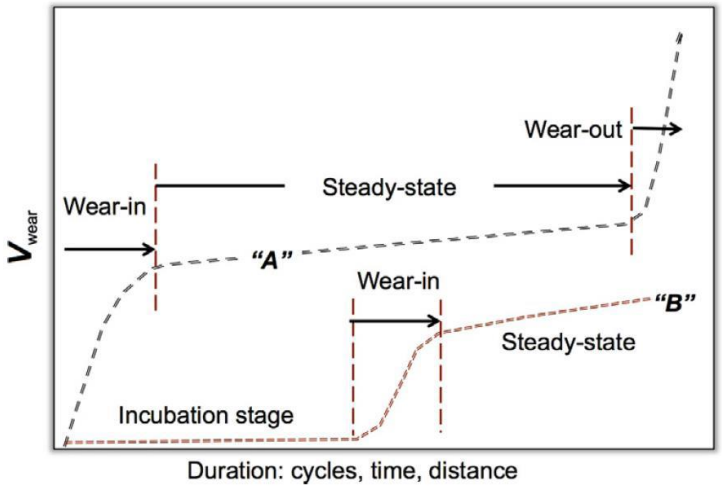


Figure 2.4. Common curves of non-linear sliding wear behaviour [77]

Typical wear behavior of sliding contact for non-induced wear transition is shown in Figure 2.4 in which they can be influenced by the material selection in a tribosystem [78]. It shows that the wear progress (Curve "A" in Figure 2.4) can be taking place at different stages; wear increases quickly through the wear-in process, development of a period of stable wear (steady-state) and wear increases again during wear-out stage. In the case of mild wear at the beginning of the sliding process (Curve "B"), at a lower normal load, the initial wear transition is likely to stay longer (incubation stage) prior to the onset of wear-in process.

The study of wear transitions requires an accurate method for in situ wear measurement. In some cases where the continuous wear measurement is impractical (due to the limitation of test rigs), some researcher chooses to stop the test rig periodically in order to measure the wear. However, this method is susceptible to a possibility of inducing an alignment error in the contact region

when reassembling the specimens for the second time. Thus, the development of a device for in situ wear measurement without disturbing the running conditions is still becoming an important area in wear research.

2.4.1. Methods for the wear measurement

Wear is involving progressive loss of material and thus, mass loss is frequently used as a measure of wear. This is performed by measuring the mass of a specimen before and after the test. Other than mass loss measurement, calculation of wear volume could also be performed based on geometry of the wear scar of a worn specimen (length and width) which can be measured by a profilometer. For example, a typical top view of wear scar on flat specimen in the case of ball-on-flat linearly reciprocating sliding wear test is shown in Figure 2.5. The total wear volume, V_w is then calculated based on the formula [79]:

$$V_w = L\{r^2 \sin^{-1}\left(\frac{w}{2r}\right) - \frac{w}{2}\sqrt{r^2 - \frac{w^2}{4}}\} + \frac{\pi}{3}\{2r^3 - 2r^2\sqrt{r^2 - \frac{w^2}{2}} - \frac{w^2}{4}\sqrt{r^2 - \frac{w^2}{4}}\} \quad (2.11)$$

Where, w is the wear scar width (m), L is the wear scar length (m) and r is the ball radius
(m).

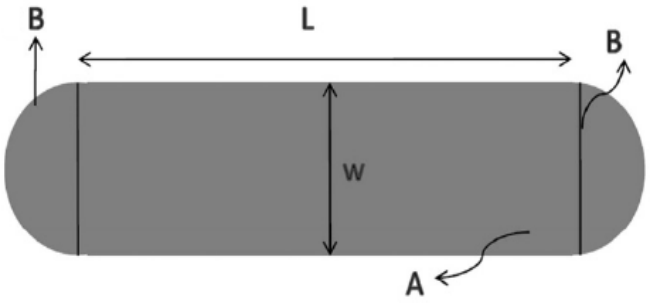


Figure 2.5. Top view of typical wear scar produced on flat specimen by ball-on-flat linearly reciprocating wear test. The calculation of wear volume is based on divided region of wear scar, A and B [79].

The use of other equipment with the aid of software could also facilitate the measurement of wear scar geometry. For example, Sharma et al. [80] proposed a method of calculating the wear volume for a ball-on-flat reciprocating sliding wear test by an optical microscopic technique. In this technique, the geometry at different positions of the worn section were

measured by focusing and defocusing on the flat surface of the sample. Although there are several methods in measuring wear, the accuracy of wear volume calculation is limited to wear scars of 'uniform' shape. In the case of the non-uniform shape of wear scar produced on the surface, the mass loss measurement method is a better choice.

2.4.2. Mechanism of wear

Wear initiates when there is insufficient protection between two contacting surfaces. The process by which wear occurs on the surfaces is commonly known as the wear mechanism. It is very important to understand and identify the mechanisms of wear before a step can be taken in order to control wear. There are four main classes of wear mechanisms namely: adhesive wear, abrasive wear, surface fatigue wear and chemical wear.

2.4.2.1. Adhesive wear

In the adhesive wear mechanism, the material is removed through a sliding process when surface asperities come into contact under a normal load. The material transfer (typically from softer to harder material) is initiated by a micro-welding process occurring at two contacting asperities when sufficient heat is generated and followed by a material shearing process (Figure 2.6) [81]. In order for the adhesive wear to take place, fracture must occur in the subsurface of one of the materials (Figure 2.7). The formation of transfer films is a characteristic feature of adhesive wear where material is transferred from one surface to another before being released as a wear particle (Figure 2.8).

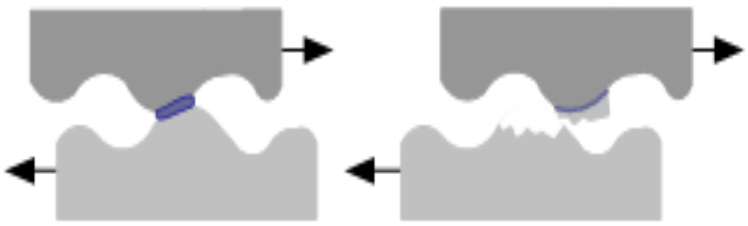


Figure 2.6. Mechanism of adhesive wear [82].

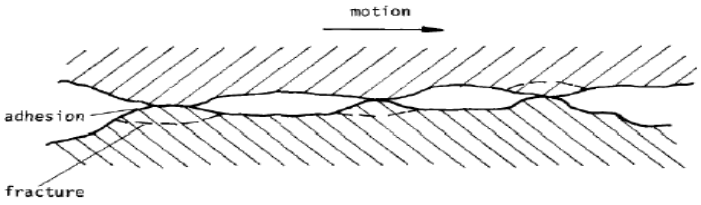


Figure 2.7. Formation of fracture in the subsurface of materials due to adhesive wear [83].

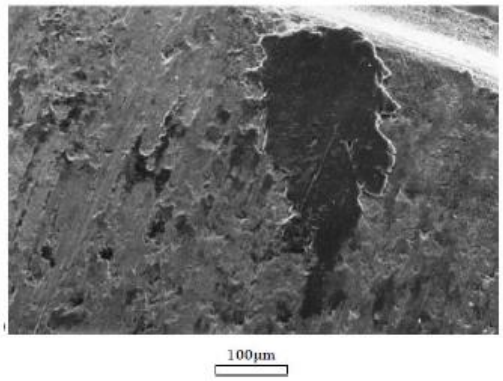


Figure 2.8. Appearance of adhesive wear example [84].

2.4.2.2. Abrasive wear

Abrasive wear occurs when hard particles (wear debris) or hard protuberances (asperities) are forced to slide on the contacting surfaces. When abrasive wear is produced by the hard particles, it is called three-body abrasive, while two-body abrasive is caused by a harder asperities penetrating into a softer material as shown in Figure 2.9. In abrasive wear, material is removed by a ploughing or micro cutting process which is influenced by factors such as particle size, shape and material hardness. A typical appearance on a worn surface caused by abrasive wear is shown in Figure 2.10.

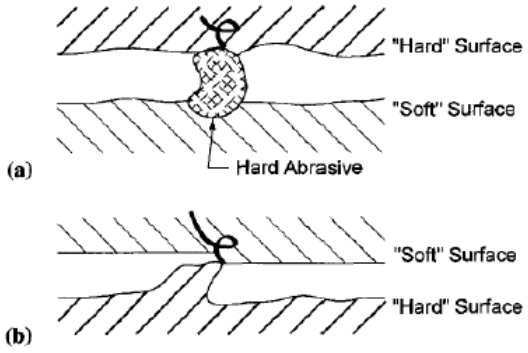


Figure 2.9. Abrasive wear model of two and three body interaction [85].

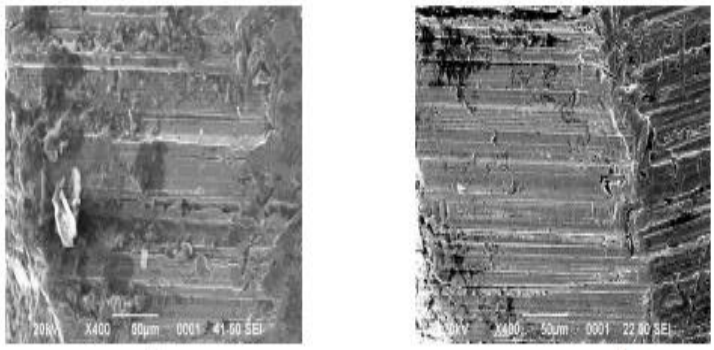


Figure 2.10. Example of abrasive wear appearance [86].

2.4.2.3. Fatigue wear

The fatigue wear occurs on the surfaces when repeated stress cycling in a rolling or sliding contact occurs. Cracks or fracture can be developed after a sufficient number of fluctuating stresses and strains as shown in Figure 2.11. Fatigue wear can be visualised microscopically by surface pitting and spalling (Figure 2.12) which are caused by subsurface shear stresses that exceed the material shear strength.

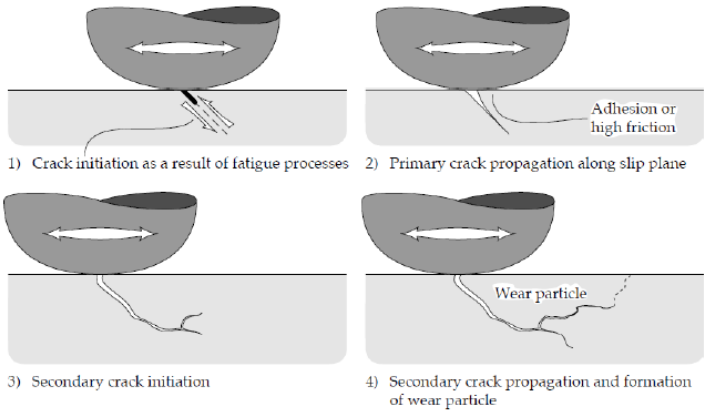


Figure 2.11. The process of surface crack initiation and propagation [87].

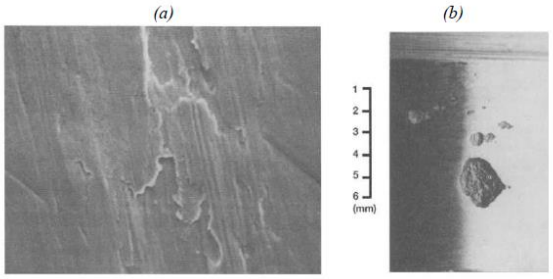


Figure 2.12. Examples wear scar appearances due to fatigue wear mechanism. (a) Spalling wear and (b) Pitting wear [88].

Another type of wear which can be categorised as a subset of fatigue wear is delamination wear as a result of subsurface cracks. In delamination theory, (Figure 2.13), dislocations are generated at sub-surface due to continuous loading. Pile-ups of dislocations then occur and lead to the formation of voids due to the inclusions (hard particles) that are contained in most engineering material. The voids will coalesce leading to cracks parallel to the surface. This ends up with the removal of a thin layer of material in the form of sheet-like laminar particle. A typical appearance on a worn surface caused by delamination wear is shown in Figure 2.14.

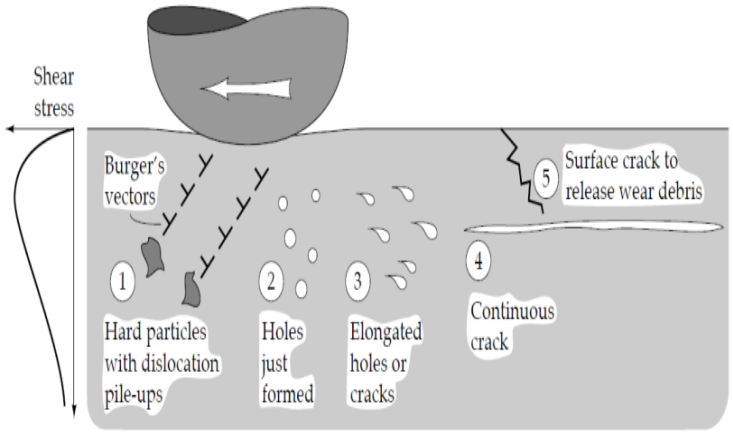


Figure 2.13. Crack formation at subsurface by growth and link up of voids [89].

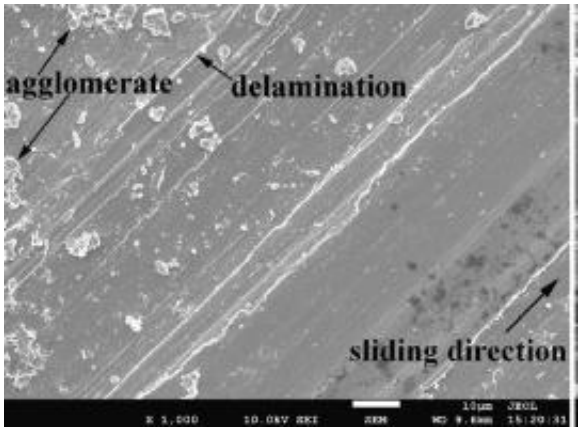


Figure 2.14. Example of delamination wear appearance [90].

2.4.2.4. Corrosive wear (chemical wear)

Corrosive wear (chemical wear) occurs when a sliding process take place in a corrosive environment. Corrosion can occur as a result of a chemical or an electrochemical reaction on the metal surfaces from the lubricant or corrosive contaminants such as salts, water and acids. The mechanism of corrosive wear is shown in Figure 2.15 in which pitting is normally produced on the worn surface. Chemical wear in air is generally called oxidative wear since the most dominant corrosive medium is oxygen. Chemical wear can be controlled by the use of appropriate inhibiting additives. An example of a worn surface due to chemical wear is shown in Figure 2.16.

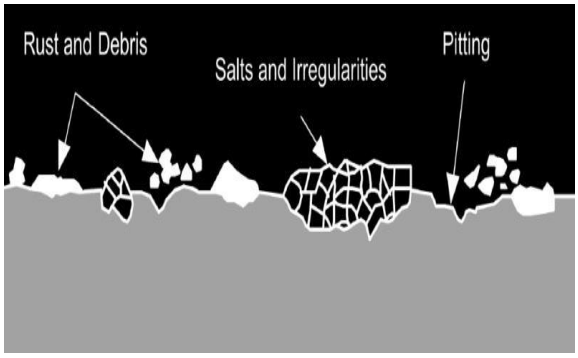


Figure 2.15. Mechanism of corrosive wear [91].

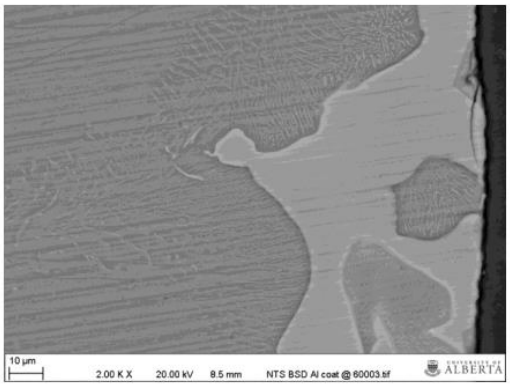


Figure 2.16. Example of corrosive wear micrograph image near the top surface of an aluminized sample [92].

2.5. Overview of lubrication and lubricants

2.5.1. Lubrication and lubricants

The main purposes of lubrication are (1) to reduce wear and heat loss that results from the contact of surfaces in motion, that is, to reduce the coefficient of friction between two contacting surfaces; (2) to prevent rust and reduce oxidation; (3) to act as an insulator in transformer applications; and (4) to act as a seal against dirt, dust, and water. A lubricant is a substance that reduces friction and wear by providing a protective film between two moving surfaces. Lubrication occurs when two surfaces are separated by a lubricant film. Lubricants are available in liquid, solid, and gaseous forms. A good lubricant exhibits the following characteristics: high viscosity index, high boiling point, thermal stability, low freezing point, corrosion prevention capability, and high resistance to oxidation.

2.5.2. Classification of lubricants

Lubricants can be classified based on the following criteria.

Physical appearance:

- Solid: The film of solid material is composed of inorganic or organic compounds, such as graphite, molybdenum disulphide, and cadmium disulphide.
- Semisolid Liquid: Semisolid liquid is suspended in a solid matrix of thickener and additives, such as grease.
- Liquid: Examples are oils such as petroleum, vegetable, animal, and synthetic oils.

Base oil resource:

- Natural oils: Oils derived from animal fats and vegetable oils.
- Refined oils: Oils derived from crude or petroleum reserves, such as paraffinic, naphthenic, and aromatic oils.
- Synthetic oils: Oils synthesized as end products of reactions that are tailored per requirement; examples are synthetic esters, silicones, and polyalphaolefines.

Applications:

- Automotive oils: Used in the automobile and transportation industry; examples are engine oils, transmission fluids, gearbox oils, as well as brake and hydraulic fluids.
- Industrial oils: Oils used for industrial purposes; examples are machine oils, compressor oils, metal-working fluid, and hydraulic oils.
- Special oils: Oils used for special purposes according to specific operations; examples are process oils, white oils, and instrumental oils.

2.6. Non-edible vegetable oil-based bio-lubricants overview

2.6.1. Resources

Some kinds of lubricants are more risky to be in contact with the environment and because of that, they must be preferably formulated with less environmentally toxic and more biodegradable products. Some pathways are already being explored such as chainsaw oil, drilling fluids, and lubricants for the train line. Other applications of highly biodegradable lubricants are in services that may contain leaking risks, like forest and mining equipment and in

very sensitive areas like platforms, agricultural equipment, and hydroelectric power plants [93].

Non-edible vegetable oils are the potential alternatives for their use as bio-lubricants due to their ability to overcome the problems related to edible vegetable oils like food versus fuel debate, environment, energy issues [94]. In addition to this, they are biodegradable as well as less toxic in nature. Moreover, they can be planted near railways, roads, irrigation canals, poverty-stricken areas, degraded forests, land unsuitable for cultivation [95]. They are well adapted to desiccate; semi-desiccate conditions and advancement in growth can be achieved without fertility and moisture. Soil enrichment through seed cakes can be achieved after extraction from oil-bearing seeds [96, 97]. Several non-edible plant oils could be considered as sustainable feedstocks for bio-lubricant production which may differ from country-wise [60]. According to the location, the oil content of the seed varies due to the difference in climate [98]. Oil content statistics and geographical locations of various non-edible plant oils are shown in Table 2.3. Among various non-edible oil-bearing crops, jatropha, karanja and neem are considered as a potential alternative among worldwide interest [99].

Table 2.3.

Oil statistics and the location of non-edible vegetable oils

Non-edible species	**Location**	**Oil content**		**References**
		Seed (% w/w)	**Kernel (% w/w)**	
Aphanamixis piolystachya (Pithraj)	Part of India and China	-	36	[100]
Azadirachta Indica (Neem)	Native of India, Malaysia, Pakistan, Burma, Bangladesh, Subtropical regions	27-32	28-48	[101]

Asclepias Syriaca (Milkweed)	Northeast and North central United States	21-26	0.017	[102]
Brassica Carinata (Ethiopian Mustard)	Native to Ethiopia	44	2.3-9.8	[55]
Balanites Acgyptiaca (Desert Date)	Native to parts of Africa and Asia	-	37-48	[103]
Bombax Malabaricum (Cotton Tree)	India	19-28	-	[104]
Carcinia Indica (Kokum)	Parts of Ethiopia and India, Tropical rain forests of Western Ghats, Konkana	46.2	-	[105]
Guizotia Abyssinica (Niger)	Ethiopia	42-60	43-50	[106]
Jatropha Curcas L. (Jatropha)	India, Philippines, Indonesia, Thailand, Pakistan	20-60	42-60	[107]
Madhumica Indica (Mahua)	Central and north India	32-50	55	[52]
Pongamia Pinnata (Karanja)	Tropical and temperate parts of Asia including India, China, Malaysia and Pacific Islands	25-50	30-55	[108]
Salvadora Oleoides (Pilu)	Arid regions of Punjab and Western India	40	-	[109]

2.6.2. Properties

Non-edible vegetable oil-based bio-lubricants have valuable and useful properties. They offer various technical privileges as compared to petroleum-based lubricants. They have high lubricity, high viscosity index, high flash point, and evaporative losses during their storage are less [110]. Generally, the physical properties of mineral oils depend on their composition in terms of carbon number distribution, and this is defined by the crude oil source. Mineral oils are composed of straight and branched chain paraffinic, naphthenic, and aromatic hydrocarbons with 15 or more carbons in a complex mixture. Accordingly, these physical properties vary widely: boiling points generally range from 300 to 600 ^{o}C, while specific gravities range from 0.820 for light paraffinic base/ process oils to just over 1.0 for high aromatic base/process oils [101, 111]. Table 2.4 mentioned about the comparison between physicochemical characteristics of non-edible vegetable oils with mineral oils.

Table 2.4.

Comparative analysis of physicochemical characteristics of non-edible vegetable oils with mineral oils [56]

Properties	**Non-edible vegetable oils**	**Mineral oils**
Specific gravity	0.87-0.93	0.92-0.99
Density range (kg/m^3)	890 to 970	840 to 920
Viscosity index	100 to 200	100
Shear rate with change of temperature	Minimum	More than Non-edible vegetable oils
Pour point (^{o} C)	-22 to +12	-15
Cold flow property	Inferior	Superior
Oxidation stability during processing and storage	More resistance	Less resistance
Corrosive by-products forming tendency in engine oil and industrial applications	Weak	Good

Flash point (^{o}C)	120-185	370-390
Pour point (^{o}C)	-10 to 6	-57 to 32
Hydrolytic stability	More prone	Less prone
Biodegradability (%)	80-100	10-30

2.6.3. Advantages and disadvantages

Based on their application, non-edible vegetable oil-based bio-lubricants have various advantages and disadvantages when considered for industrial and machinery lubrication.

According to their positive aspects, they are non-toxic and environmental friendly. They provide superior lubricity, which results in a better life of the equipment, minimized corrosion of metal surfaces, safety on industrial shop floors due to higher flash point and a high viscosity index. For example, the viscosity index for non-edible vegetable oil is approximately 220 and for most of the mineral oils, it is in the range of 90-100. Their high viscosity also minimizes operating temperature and results in saving of approximately 16% energy or more. These bio-lubricants have higher heat content, minimum Sulphur content and are biodegradable. Non-edible vegetable oils, a renewable resource, are finding their way into lubricants for industrial and transportation applications. Waste disposal is also of less concern for vegetable oil-based products because of their environment-friendly and non-toxic nature. Oleo chemical esters are a class of products that improve the thermal and cold-flow instability of the neat non-edible vegetable oils and fulfill the basic requirements as lubricant base stocks. Among the esters used for the production of bio-lubricants are the polyol esters such as tri-methyl propane (TMP), penta-erythritol (PE), and neopentylpolyol (NPG) [50]. These bio based esters deliver good low-temperature fluidity and although they cannot be used at high temperatures, they can be suitable in less extreme applications [112].

Biofuels have already been accepted around the world for their merits over conventional petroleum fuels, including the opportunity for energy independency. Now, similar growth is expected for bio-lubricants, which are derived from renewable non-edible vegetable oils for different niche applications. Recently, the idea of producing non-edible vegetable oil-based

bio-lubricants has led researchers to develop process technologies for their commercialization. Bio-lubricants are esters of heavy alcohols derived from vegetable oil-based feedstock and have lubricating properties similar to those of mineral oil-based lubricants. Even though bio-lubricants are priced twice as high as conventional petroleum lubricants, industries are investing in R&D toward increasing oil recovery from seeds, reducing the costs of processes and exploring niche application areas. Table 2.5 shows various beneficial properties of non-edible oil-based bio-lubricants.

Table 2.5

Beneficial properties of non-edible oil-based bio-lubricants [103].

Benefits	**Applications**
Improved lubricity	Minimum friction losses, energy saving from 5% to15%
High viscosity index	Suitability for high temperature applications, 250^0C or above
Lower volatility	Reduction in exhaust emissions
High flash point	Safety on industrial floors
Improved skin compatibility	Less dermatological problems
Oil mist reduction	Less inhalation of mist or vapors
Rapid biodegradation	Reduction in toxicity and environmental hazards
Higher boiling temperatures	Reduced emissions
Higher detergency	Remove the use of detergents as additives

As per the negative aspects, non-edible oil-based bio-lubricants have low oxidation stability in their natural form. Although bio-lubricant produced from non-edible vegetable oil has some demerits, such as inferior storage, high feedstock cost, low pour point, low evaporation rate, low heating value and poor cold flow properties during their use in a colder climate. These oils are mainly triglycerides. The glycerol fragment contains three hydroxyl groups esterified with carboxyl groups of fatty acids. Excessive of saturated long chain fatty acids

leads to poor low-temperature behavior, while an excess of certain polyunsaturated fatty acids leads to unfavorable oxidation behavior. Even very long monounsaturated fatty acids worsen the low-temperature behavior. The triglyceride structure gives these esters a high natural viscosity (and viscosity index) and is also responsible for structural stability over reasonably operating temperature ranges. The flash point is high, which correlates to a very low vapor pressure and volatility, thereby reducing or eliminating potential hazards during use. Even so, they have poor oxidative stability as compared to mineral oils and in general, they cannot withstand reservoir temperatures over 80 °C. However, the use of appropriate antioxidants can combat this. These oils are also less hydrolytically stable, foam more and have lower filterability than comparable mineral oils. They have an unpleasant smell, are not compatible with paints/surface coatings and causes clogging of filters [113]. Oxidation stability and low pour point were improved by partially adding additives and using N-Phenyl-alpha-naphthylamine as an antioxidant to improve oxidation stability [114].

Moreover, transesterification or epoxidation are the solutions to meliorate oxidation stability at low temperature. To make vegetable oil-based lubricant sustainable, there is a need to improve its narrow range of viscosities [115]. Viscosity is one of the significant factors in determining the coefficient of friction between the sliding surfaces as it acts as a protective film between the surfaces in contact to protect them from wear [116]. To do so, viscosity modifiers, which are friendly with the environment, can be used. Oleogels (conventional bio-based lubricant) and ethylene-vinyl acetate (EVA) copolymers have been developed. It was observed that EVA acts as an effective thickening agent to make vegetable oil bio-based lubricant [117]. The viscosity of a bio-based lubricant can also be increased by using ethylene-vinyl acetate and styrene-butadiene-styrene copolymers as they increase the kinematic viscosities at 40ºC and 100ºC temperatures [118].

2.6.4. Applications

Non-edible oil-based bio-lubricant has various applications related to industrial and machinery lubrication due to their enriched inherent qualities. Due to their less toxicity and environmental sensitivity, they found a wide range

of applications. Some of the examples of applications are transmission fluids, gearbox oils, hydraulic fluids turbine and compressor oils, chainsaw oil and special type like instrumental oils. Bio-lubricant can replace mineral oils as gearbox oil, hydraulic oils, engine oils, lubricants for 2 stroke engine, tractor, insulating oils, aviation oil, grease, metal grinding oils or multipurpose oils [119].

2.6.5. Biodegradation/eco-friendliness

Lubricant manufacturers are facing several challenges in preparing for an anticipated boom in demand for biodegradable lubricants and hydraulic fluids. The effort promises major benefits in providing users with a new generation of environment friendly products.

Awareness is growing on the benefits of biodegradable lubricants. To develop these eco-friendly base stocks, many approaches are being studied. Five types of biodegradable base stocks are currently available to the manufacturers who want to produce eco-friendly lubricants. These are:

- Highly unsaturated or high oleic vegetable oils (HOVOs),
- Low viscosity poly alpha olefins (PAOs),
- Dibasic acid esters (DEs),
- Poly alkylene glycols (PAGs),
- Polyol esters (PEs).

For each of them, it must be considered whether biodegradability is a realistic concept, technically feasible, environmentally necessary and cost-efficient concept.

Vegetable oil-based lubricants based on renewable sources, such as corn, soybeans and rapeseed has eased dependence on foreign sources of imported petroleum. They have less potential toxicity and degrade more readily in the environment. Biodegradable lubricants and hydraulic fluids based on these will be widely available in the United States. Genetic engineering efforts yield vegetable oils with improved lubricating properties that are superior to mineral oils. These include genetically modified corn and soybean oils with high oleic content that enhances oxidation stability.

Synthetic lubricants whether synthetic hydrocarbon, organic ester are facing the same daunting problem. Mineral oil-based lubricants are cheap and

plentiful. So, the question arises of how to convince industrial users to pay triple, quadruple or even scores more per pound for a synthetic product. One can justify it from the standpoint of performance, warranty costs, avoiding early failure of the part, etc. despite evidence that costs can be cut by switching to synthetic lubricants. Their needs are so simple and petroleum oils and greases are so cheap that synthetics cannot compete for these applications, despite a widespread impression among industrial users that in general, synthetic lubricants protect well, last longer and outperform their conventional counterparts. Thus the conventional lubricants are strongly entrenched. However, the upcoming finished lubricant quality specifications because of their improved performance to meet future's stringent environmental regulations are the main driving force for new technological developments [120].

Lubricants find their way into the environment through various means during handling and application including through evaporation, exhaust fumes, faulty operation of equipment, and improper disposal. Environmental authorities have become conscious of the effects on the flora and the fauna, signifying the importance of the biodegradability of lubricant products. Biodegradability measures the environmental fate of a lubricant component, its decomposition mechanisms, and the possible environmental impact during any stage of its deterioration. Evaluation of the biodegradability of lubricating oils using standard test procedures provides a better knowledge of how the chemical structure influences the biodegradability of lubricants. The OECD is a prominent body that promotes policies to improve the economic and social well-being of the people in member countries. It facilitates common forums in which member governments can work together to share experiences and seek solutions to common problems [121].

The selection of a test procedure for evaluating ultimate biodegradability is difficult since most lubricating base oils do not dissolve in water. The situation is even trickier when biodegradation in soil has to be evaluated. Studies have shown that lubricants based on mineral oils are least biodegradable in soil relative to synthetic oil- and vegetable oil-based formulations. In general, the rate of degradation of all lubricants, including

natural vegetable oil, in soil was very slow, taking more than a year to generate extractable residues. Besides, the effects of contamination by different oils on growth rate and yield of spring wheat varied from small reductions to complete inhibition of seed germination [122]. All lubricants exhibit common behaviours such as poor solubility and low density. These oils form a layer on the surface of the water reducing oxygen exchange, resulting in depletion of dissolved oxygen. Whenever a spill occurs, the physical and chemical properties of spilled substance determine its fate in the environment. In the case of vegetable oils, the problem is aggravated by their high biological oxygen demand (BOD) during biodegradation. Further, highly viscous oils contaminate feathers of birds and furs of mammals, resulting in loss of buoyancy and alterations in metabolism [123].

Biodegradability gives an account of the environmental fate of a substance and its susceptibility to biochemical breakdown by the action of microorganisms. Since lubricants are insoluble, have less density than water, and are hydrophobic, they spread on the surface of the water. The degradation process of lubricant begins with the action of microorganisms and it is first transformed into carboxylated or hydroxylated intermediates that are soluble in water. This leads to the disappearance of the visible oil slick on the surface of the water. This primary biodegradability is measured using CECL-33-A-93 standard test. In this method, the extent of disappearance of *C–H* stretching vibrations from the infrared spectrum of the test sample is measured. The method was primarily developed for two-stroke engine oils and relevant only for German environmental label. As the primary degradation only accounts for the disappearance of the parent compound, it does not necessarily imply that the compound has completely degraded. The other limitation of this test is that it does not differentiate between primary and ultimate degradations

To evaluate the persistence of test material in the environment, it is necessary to determine how readily the biodegradation process occurs. Simple test methods where microbes have the opportunity to acclimatize to the substrate are used for evaluating ultimate biodegradability. The OECD 301B method measures the amount of CO2 evolved from a flask containing the test substance for over 28 days and compares it to the theoretical value based on the

total organic carbon content of the sample. In reality, complete biodegradability will not happen in the OECD 301B test because a portion of the substrate is always converted into biomass. A substance is considered as readily biodegradable if the conversion after 28 days is more than 60% and if 50% biodegradation occurs within 10 days. A few other test procedures, such as ISO 10708 and 14593, are also used to evaluate biodegradability. Vegetable oils are not expected to bio accumulate since the ester group is easily susceptible to enzymatic cleavage and the derivatives are metabolized. Among the non-plant derivatives, synthetic esters also have high biodegradability; whereas PAOs are better than mineral oils because of their higher degree of linearity Biodegradability in seawater is important for the lubricant context as mineral oils, synthetic esters, and PAO are used in offshore drilling equipment and are mainly transported in ships. In the case of offshore drilling equipment, some portion of the lubricant is always left on the seabed after separation from the drilling fluid, leading to contamination. Two standard methods based on the OECD closed bottle test (OECD 301D) and the modified OECD screening tests (OECD 301E) are used for this purpose. These differ from the conventional test procedures in that no inoculum is added and biodegradation occurs by the action of bacteria present in the seawater. The use of a high concentration of test substance in these tests means that the tests do not mimic the conditions normally present in the marine environment [124]. Other tests, such as the Oslo and Paris Commission ring test, are equally valid for evaluating the biodegradability of chemicals in seawater. Studies have shown that readily biodegradable substances in freshwater also biodegrade in seawater, but at a slower rate. With this background, the European Centre for Ecotoxicology and Toxicology of Chemicals recommended a new dosing procedure. In this method, the test duration was increased from 28 to 60 days. It was observed that the extended incubation periods tend to decrease test precision. It also recommended making a hazard assessment of lubricants in seawater using data from freshwater tests [125, 126]. Table 2.6 shows the biodegradability of some base stocks. The environmental toxicity of lubricating materials depends on the base oils and additives used in their production to enhance their property [11].

Table 2.6**.**

Bio-degradability of some base stocks [93, 120]

Lubricant type	**Range of biodegradability (% loss at 21 days)**
Aromatic esters	0-90
Alkyl benzenes	5-20
Polyols	5-95
Polyethylene glycols	10-75
Mineral oils	15-75
Diesters	55-95
Non-edible vegetable oils	70-100

Biodegradability depends on certain factors which are responsible for the change in the chemical structures of organic compounds such as air, humidity, pressure, and temperature. Biodegradability of lubricating materials depends on the changes in the property of chemical structure during their use [103]. ASTM test method D 5864 determines lubricant biodegradation. Mineral oils are complex mixtures of thousands of different compounds with a wide molecular weight distribution, but they are mainly hydrocarbons including paraffin's (linear alkanes or waxes, and branched alkanes), alicyclic and olefinic species, aromatics and polycyclic aromatics (PCAs) or polycyclic aromatic hydrocarbons (PAHs). The latter are environmentally harmful. This has limited the application of naphthenic base oils to less than 10% of total mineral oils. Non-renewable petroleum base oils, primarily composed of hydrocarbons (paraffinic, naphthenic and aromatic structures), lack chemical functionality. Biodegradation of thirty-two mineral oil-based on paraffinic nature was investigated using the CEC L-33-A-93 test. Biodegradation level of the oils tested lies in the range 15% to 75% are acceptable according to the environmental compatibility. With an increase of aromatic/or polar compounds in the tested fuels, biodegradability increases. Biodegradability decreased as a function of the kinematic viscosity (KV), the pour point, the flash point (FP)

and the refractive index (RI), which was higher than that of non-edible vegetable oils. Linear relationships between biodegradability and FP or RI values were observed. These results show that, besides chemical features such as the contents in polar and aromatic compounds, simple physical quantities such as KV, commonly used to characterize lubricant properties, may be useful parameters for predicting the biodegradability of mineral base oils [127]. Figure 2.17 shows the schematic image of non-edible and mineral oil life cycles depicting relevant material.

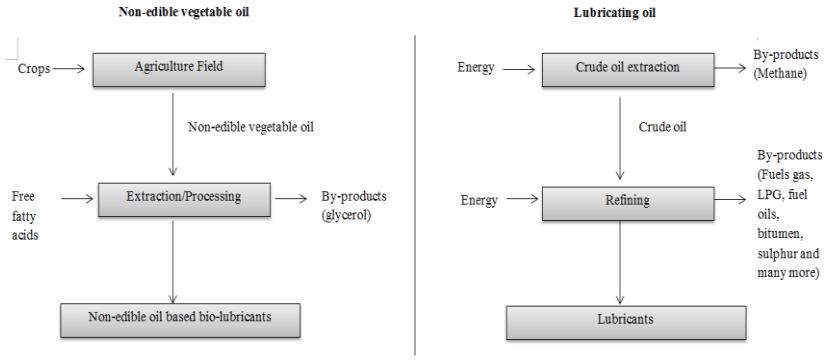


Figure 2.17. Schematic image of non-edible and mineral oil life cycles depicting relevant material.

2.7. Prospects of non-edible vegetable oil-based lubricants as alternatives

There are numerous valuable and important physicochemical properties offered by non-edible vegetable oil-based lubricants which provide various technical privileges over mineral oils. It includes high lubricity characteristics, high viscosity index, and minimum evaporative losses during transportation. Table 2.7 shows the physiochemical properties of various non-edible vegetable oils. Various research projects have been developed and completed by researchers to improve the physiochemical properties of non-edible vegetable oil-based lubricants. These studies revealed that non-edible vegetable oil-based lubricants can become efficient and inexpensive substitutes to the mineral oils. The summary of the research work conducted by various researchers is shown in Table 2.8.

Table 2.7.

Physicochemical properties of various non-edible vegetable oils.

Oils	Cloud point (^{o} C)	Pour point (^{o} C)	Flash point (^{o} C)	Viscosity at 40^o C (N.s/m^2)	Density (kg/m^3)	Oxidation stability, (s)	Ref.
Camellia Japonica and Vernicia Fordii	11.7	4.1	147	3.7	882.6	-	[111]
Guizotia Abyssinica	1.4	-7	152	4.1	-	-	[128]
Idesia Polycarpa var. Vestita	3.8	-8	128	5.9	863	11484	[57]
Madhuca Indica (Mahua)	4.7	6	134	3.92	908	35856	[129]
Nicotiana Tabacum (tobacco)	-	-	161.2	4.34	891	-	[96]
Pongamia Pinnata (Karanja)	-	-	173	4.8	893	2664	[116]
Ricinus Communis	-13.1	-	156	15.4	907	1116	[130]
Sapium sabiferum	-	-	62	19.4	877	-	[50]
Jatropha Curcus L.	-	0.18	164	7	881	2052	[106]

Table 2.8.

Non-edible oil-based lubricants.

Non-edible based lubricants	Reference Lubricant	Test Method	Result	Ref.
Cottonseed oil	SAE 40	Pin on disc machine	Less wear at high speed and load High lubricity Less coefficient of friction Eco-friendly Biodegradable	[131]
Jatropha oil	SAE20W40	Pin on disc machine	Lesser frictional losses Less wear Lesser aggregate weight loss	[132]
Mongongo oil	SAE20W40	Four ball wear tester	High viscosity index Less deposit forming tendencies Less coefficient of friction	[133]

Jatropha oil	SAE20W40	Pin on disc machine	Less wear scar diameter Minimum specific wear rate at high velocity	[58]
Pongamia oil	SAE20W40	Pin on disc machine	Less surface wear Minimum degradation of lubricant at all applied loads	[116]
Pongamia oil	SAE20W40	Four stroke, Single cylinder, direct injection CI engine	Efficiency improvement Lower frictional losses Improvement in BSFC and BTE at medium and high load condition	[134]

Non-edible oil-based lubricants can provide improved lubricity in comparison to crude mineral oils by doing improvement in the limitations. They can also show positive characteristics due to which they will become popular. It has been concluded through research that tribological properties could slightly be improved with an increase in temperature [14]. Some researchers have studied the wear behavior of various non-edible oil-based bio-lubricants using several tribometer techniques. Investigation on friction and wear characteristics

of the jatropha oil blended in different proportions considering mineral oil as a reference was conducted. The reference mineral oil is SAE20W40. The finding shows reduced wear and coefficient of friction in the case of jatropha oil blended with the reference lubricant (maximum 10%) [135]. An alternative to the existing oil-derived lubricant production has been investigated by providing the market bio-lubricant synthesis catalyzed by enzymes. Moreover, the use of bio-lubricant to develop a higher added-value product is a very attractive solution for bio-lubricant production manufacturers in extending their production supply and the potential sales markets, especially in the East Europe region [136].

The wretched biodegradability of crude oil-based lubricants motivates the industry to develop a suitable eco-friendly lubricant from agriculture feedstock [15]. Utilization of mineral oils includes area like hydraulic oils, metal working fluid, transmission fluids, and gearbox oils. The products from non-edible vegetable oils such as jatropha, karanja, mahua, castor, jojoba, polanga show improved lubricity or similar trend in comparison to petroleum-based products apart from being less costly. It has been reported that properties such as viscosity, oxidative stability, lubricity, and deposit formation tendency of biodegradable lubricants. Their findings reveal that they have a high viscosity in comparison to synthetic oil-based lubricants [44]. Apart from this, they are from renewable resources, biodegradable, non-toxic and eco-friendly in comparison to petroleum-based mineral oils. The reason for this was the addition of 88% castor oil with ricinoleic which shows improvement as compared to refined mineral oil and high oleic sunflower oil.

Furthermore, non-edible based lubricants are less volatile due to the higher molecular weight of the triacylglycerol molecule. With the increase in temperature, viscosity only shows narrow changes. They can be considered as an alternative to petroleum-based mineral oil due to certain inbuilt technical properties and also they are biodegradable as well as less toxic in nature. Furthermore, they have high lubricity, high viscosity index, high flash point and less evaporative losses. Tribological behavior of bio-lubricants and bio-lubricant contaminated lubricants using a pin on disc tribometer was investigated [112, 125]. The pins were prepared by alloying top compression ring material with white cast iron and a casting process was used for alloying

the disc with white cast iron material of engine cylinder liner. Lubrication oil samples being used for the analysis were 10% bio-lubricants, 10% B20 R with SAE20W40 commercial lubricant, 10% diesel with SAE20W40 commercial lubricant and SAE20W40 commercial lubricant. The use of bio-lubricants resulted in a reduction of the coefficient of friction as well as wear. During similar operating conditions, bio-lubricants provide improved lubricity than any other samples. Moreover, surface wear was less for the bio-lubricant and bio-lubricant contaminated lubricant samples in comparison to diesel contaminated lube oil. The substitution of petroleum-based synthetic lubricant with rapeseed oil-based bio-lubricant in a variable compression ratio diesel engine was explored. Rapeseed oil-based bio-lubricant was formulated through chemical modifications like epoxidation, hydroxylation and esterification process for improving its thermo-oxidative stability and cold flow properties. The Nano CuO (copper oxide) an anti-wear Nano additive was added to chemically modified rapeseed oil to improve anti-wear behavior. A marginal improvement in brake power, brake thermal efficiency, and mechanical efficiency was observed with the use of rapeseed oil-based bio-lubricant which can be attributed to higher lubricity of rapeseed oil-based bio-lubricant. Ferrogram revealed a reduced Fe, Al and Cu wear for bio-lubricant/bio-lubricant combination, suggesting inherent lubricity of rapeseed oil as biofuel and bio-lubricant [44].

An experiment was conducted on a commercial four stroke, single cylinder, and water cooled, direct injection diesel engine to investigate the performance of bio-lubricant (Pongamia oil) as a substitute for mineral oil [134]. It has been concluded that neat pongamia oil provides minimum brake specific energy consumption and highest brake thermal efficiency at medium and high load conditions due to the low viscosity of pongamia oil lubricant. Less frictional losses were observed for all fuel variants and pongamia oil lubricant as compared to mineral oil. Synthesis and tribological properties of bio-lubricant using epoxy canola oil using sulfated Ti-SBA-15 catalyst were investigated. Sulfated Ti-SBA-15 demonstrated 100 % conversion of epoxy canola oil to the esterified product (bio-lubricant). Langmuir–Hinshelwood–Hougen–Watson type reaction mechanism was proposed, and the reaction

follows a pseudo-first order. The tribological properties of bio-lubricant such as oxidative induction time, cloud point, pour point, and kinematic viscosity at 100 °C were measured. Prepared bio-lubricant demonstrated the excellent lubricity property [137].

The activity of solid base catalysts with selected dopants on the synthesis of trimethylolpropane triesters (TMPTE) bio-lubricant from palm oil methyl esters (POME) was performed. The type of metal oxide and mixed metal oxides demonstrated a significant effect on the physical property of the catalyst and its catalytic activity [42, 138]. A statistical experimental design with response surface methodology (RSM) was implemented to optimize the experimental conditions and to understand the interactions among the process variables. At the optimum conditions, maximum epoxide content was found to be 5.8 mass% [105].

The properties of WCOME and its epoxide were determined by standard methods and compared. Characterization results revealed that the structurally modified WCOME epoxide had improved viscosity and thermo-oxidative stability compared with unmodified WCOME. Overall, outcomes indicated that prepared epoxide can act as an alternative lubricant base stock for various industrial applications [139]. The tribological behavior of M30NW stainless steel against ultra-high molecular weight polyethylene (UHMWPE) was investigated. The friction coefficient and wear volume of UHMWPE were examined. It is found that under oil lubrication, the friction and wear behaviors of UHMWPE were the best. Morphological and chemical studies of the worn surfaces were conducted and wear mechanisms were proposed. The observed performance of natural oils was linked to their chemical composition and their adsorption ability to the stainless steel. The purpose of this work was to utilize commercially available palm oil and jatropha oil for the production of bio-lubricants, through two stages of trans esterification. The first stage is the process of using methanol in the presence of potassium hydroxide to produce bio-lubricant. The second stage is the reaction of bio-lubricant with trimethylolpropane using sodium methoxide as a catalyst to yield palm or jatropha oil base trimethylolpropane esters (bio-lubricants) [139]. The obtained jatropha oil-based trimethylolpropane esters exhibited high viscosity indices

(140), low pour point temperature (-3^0 C), and moderate thermal stabilities and met the requirement of commercial industrial oil ISO VG46 grade. In spite of the high pour point of Palm oil-based trimethylolpropane esters (5^o C), which needs pour point depressant to reduce the pour point, other lubrication properties such as viscosity, viscosity indices, and flash point are comparable to commercial industrial oil ISO VG32 and VG46. Globally the volume share of biodegradable/eco-friendly lubricants is around 15% and it is predicted that it will contribute around 30% in upcoming 10 to 15 years. Various changes within next 5 years to 10 years will be faced by world lubricant market and certainly remain an interesting field [140].

2.7.1. Jatropha and Pongamia oil as an alternative bio-lubricants

The oil producing plants, such as soybeans, palm trees and oilseeds like rapeseed can produce compounds similar to hydrocarbon petroleum products. Utilizing edible oils for bio-lubricant production is under debate as they compete with food. Therefore, the focus is now towards the use of non-edible oils such as jatropha, pongamia, sea mango and algae oil, waste cooking oils, low-quality animal fats and side-streams from oil refining as feedstocks for bio-lubricant production [141].

Jatropha curcas L. (JCO) is a native crop in North and Central America and it is now widespread all over the tropical and subtropical world such as; Africa, India, South-East Asia and China. This plant is drought resistant, perennial, and can grow in rocky lands, marginal lands, deserts, and even in saline soils. Jatropha oil content in the jatropha seeds is about 300–400 g/kg [52, 106, 142-144]. Presence of some toxic components such as; phorbol esters, the high content of stearic acid and free fatty acids (FFAs) hinder JCO from using for edible purposes. Jatropha oil contains mainly linoleic, stearic, oleic, palmitic and arachidic acids that can be converted to their methyl esters during the transesterification reaction and form bio-lubricant [52, 97].

Karanja is also called *Pongamia Pinnata*. It is a medium size tree; easy to grow and becomes an adult in four to five years. It can survive in heat, drought, salinity and frost conditions. It is a monotypic genus grows abundantly along coasts, riverbanks and reclaims marginal lands but it requires full overhead light in early stages [108, 145-149]. In India, it found from Himalayan

foothills to Kanyakumari. At many places, its seeds remain unused. Karanja fruits have viability period of one year; seeds number varies between 9–90 kg per tree. Karanja pods are elliptical in shape and contain a single seed. Pods are 2–3 cm wide and 3–6 cm long with thick walled. Karanja seeds are brown and 10–20 mm long. Karanja Seed has 27–39% of the oil. The presence of toxic di-ketone pongamol and Karanjin in Karanja oil makes it non-edible oil [149].

Hence, Jatropha and Pongamia oil are one of the most appropriate sustainable alternative feedstock for bio-lubricant production in terms of availability and cost. Despite of having lots of advantages of bio-lubricant over petroleum based lubricant, the attempt to formulate the bio-lubricant and its applications are very few. Further systematic research that confirms the tribological behavior of different bio-lubricant blends was not reported. In this study, tribological behavior of different bio-lubricant blends has been performed and it has been correlated with the wear of piston wear during the operation of diesel engine [142].

2.8. Lubricant market and current status

2.8.1. Worldwide lubricant demand

In 2004, 37.4 million tons of lubricant were consumed which includes the maximum contribution of automotive lubricants 53%, industrial lubricants 32%, process oils 10% and remaining 5% marine oils. In 2005, 37.9 million tons of lubricant consumed worldwide in which Asia-Pacific region dominates North America for lubricant consumption. The Overall growth rate was around 0.8 % during 2007, and the consumption was 41.8 million tons. Limited data are available for the year 2008. A forecast was there that the global lubricant demand was to reach 40.5 Mt in 2012 which is lower than in comparison to an earlier forecast of 41.8 Mt in 2010 [150]. World demand for lubricants is going to increase predictively 2.3 percent per year to 43.9 million metric tons in 2017 [119].

World demand for lubricants is projected to rise 2 % annually to 45.4 million metric tons in 2019. The fastest gains are expected in the Asia/Pacific region, where an expanding number of motor vehicles in use and continued industrialization in large countries such as China and India will support rising demand. Developing regions such as Central and South America and the

Africa/Mideast region will also exhibit healthy gains in response to economic growth, rising manufacturing output, and increasing motor vehicle production and ownership rates. More mature markets, such as the United States, Western Europe, and Japan, are expected to stay fairly flat, as the greater availability of premium lubricant products with longer drain intervals will restrain growth [35, 151]. Additionally, many of these developed countries enforce strict regulations on the use and disposal of lubricants, which will drive demand for nonconventional lubricants, such as more environmentally friendly bio-based lubricants and lubricants derived from re-refined base oils [13].

The fastest growth will be in Asia, supported by rising vehicle ownership rates and ongoing industrialization in large countries such as China. Above average increases will also occur in South America, the Middle East, and Africa. These regions will each experience healthy economic growth, rising manufacturing output, and expanding motor vehicle parks; all of which will support lubricant consumption. In contrast, demand will remain nearly flat in the developed countries of North America and Western Europe, where efficiency gains will offset the effects of rising economic and industrial output. US demand for synthetic lubricants and functional fluids are estimated to increase 6.8 percent per year to $6.3 billion in 2018, with volume rising to 2101230 m^3. Growth will result from increasing market penetration of synthetic products at the expense of conventional fluids, driven by environmental concerns, user preferences, and increasingly stringent requirements for lubricant and fluid performance. The outlook for synthetic products will vary across markets and applications, with each product subject to a unique set of factors influencing demand [152-154]. Figures 2.18 and 2.19 present the lubricant global market according to the application area and geographical data, respectively [119]. These include world markets and the segmentation by region and application area, respectively in percentage. Table 2.9 present the forecast lubricants demand by region, up to 2020. About 1.5 million tons per year of capacity has closed over the past two years, and a further 1.1 million t/y will be shuttered in the first half of 2016. A large number of previously announced projects have been postponed to after 2020, if then. Or they have been cancelled altogether. A multitude of issues prompted these decisions.

For example, low crude oil prices have sharply curtailed capital expenditure programs among integrated oil companies. In addition, the large oversupply of base oils shows little sign of abating in the near-to medium term, affecting some oil companies. Another factor is the sanctions against Russia that have limited access to capital and technology for some companies as Gazprom Neft and Zarubzehneft. Also, U.S. rerefiners have been affected by depressed prices and margins, especially for Group I and II light neutrals.

Finally, low crude oil prices led to reduced access to high-cost, waxy crudes that HollyFrontier had planned for Group III+ base oils production. And there will probably be more cancellations to come. Over the past 2 years, over 4 million t/y of previously announced capacity additions have been delayed, some indefinitely, or cancelled altogether. Only 800,000 t/y of those may still be possible prior to the end of the decade and another 650,000 t/y of projects to upgrade Group I to Group II and III have been pushed back by a couple of years, possibly longer. As a result of the delays and cancellation, the latest forecast shows a marked reduction of capacity additions from just two years ago, and the timing and size of the original 2014-15 "tsunami" has abated somewhat. Nevertheless, 17 major capacity additions are still possible by 2020. Five came on-line in 2015, representing 1.1 to 1.2 million t/y. Five more are awaiting start-up or are under construction for streaming during 2016, totaling 2.2 million t/y. Another four may add 800,000 t/y in 2018 or 2019. And three were announced for late in the decade, representing 2.5 million t/y. Pulling it altogether and adding PAOs, naphthenics, some smaller projects and the retrofit grade shifts, and then throwing in the inevitable capacity creep. We could end up with a further 9.5million t/y of additions by the end of 2020, against a backdrop of little or no increase in demand. That's the bad news. This year will be another big year, with 2.7 million t/y of additions. There will be a respite in 2017, and another surge is possible in 2018. Additions will be predominantly Group II in Asia and Europe for use in higher tier formulations and to supplant supply lost from Group I closures. Today, the surplus is about 5 million t/y, and the loss has been limited only by five recent closures and an industry plant utilization of

about 70 to 75 percent. By the end of the decade, the surplus could grow by more than 6 million t/y, necessitating further closures [26, 33].

Finally, some Group I plants are already operating near their lower continuous limits. The migration away from Group I continues, with Group II rapidly becoming the workhorse quality. Reviewing the regional production profiles likely in 2020 that Asia will become the largest producer of all three paraffinic qualities. Group II will more heavily dominate the North American and Asian regions, and South America will continue to be constrained to Group I. All regions will experience declines in Group I supply, he related, but they will be most pronounced in Europe. But Europe and the Middle East should see their first major production of Group II. Project delays and cancellations will keep South America as a large, growing importer of Group II. North America and Asia will continue to be the Group II supply sources to the other regions. Only relatively minor increases are expected in existing production of Group III. The Americas will remain almost wholly reliant on imports of this base stock, primarily from Asia and the Middle East [155-158].

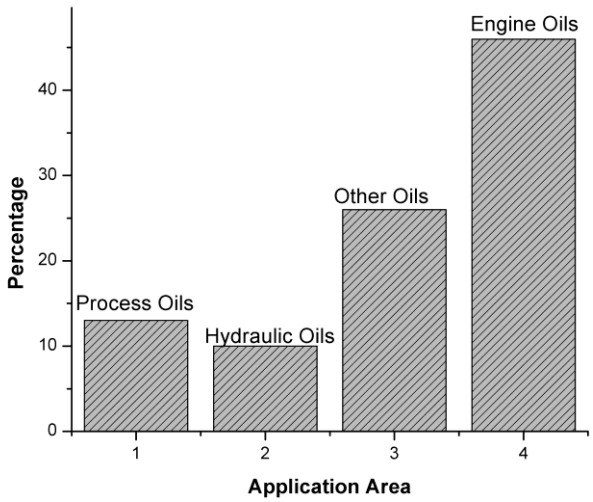


Figure 2.18. Global lubricant market according to the application area [119].

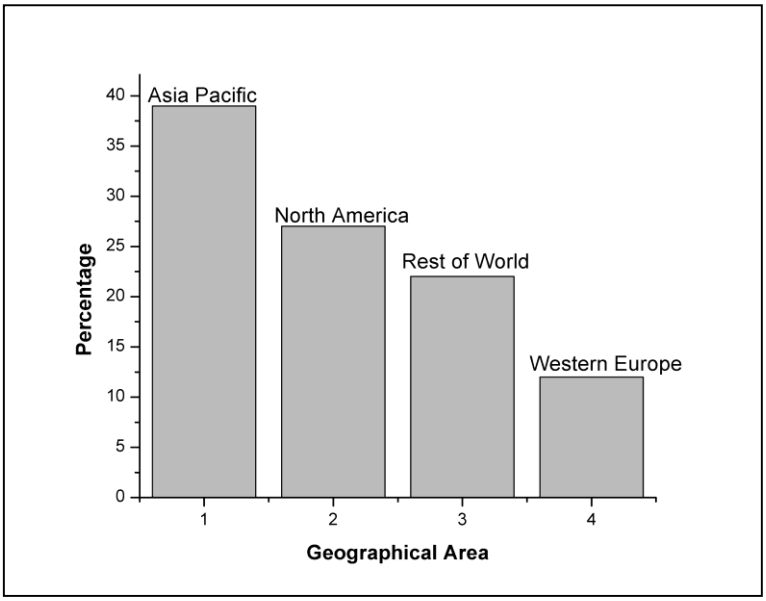


Figure 2.19. Global lubricant market according to the geographical area [119].

Table 2.9.

Forecast lubricants demand growth by region up to 2020 [159-161].

Geographical area	**Million tons/year**		
	Group 1	**Group 2**	**Group 3**
Asia Pacific	5.2	12.5	4.2
Central & South America	1.1	-	0.1
North America	1.8	8.8	0.1
Middle East & Africa	2.1	1.3	1.7
Central, Eastern and Western Europe	4.9	2.2	1.2

2.8.2. Global status of lubricant manufacturers

Globally there are approximately 1700 small and large lubricant manufacturers. Approximately 300 of these manufacturers are located in Europe. Furthermore, there are 380 blending and packaging plants in Europe. These are vertically integrated petroleum companies (Shell, BP Castrol, Exxon Mobil etc.) dealing with exploration, extraction, and refining of crude petroleum oil. Approximately 1,200 independent lubricant companies concentrate on manufacturing and marketing of lubricants that includes application products

like transmission oils, gear oils, and hydraulic oils. Table 2.10 shows the top 12 global lubricant manufactures worldwide available.

Table 2.10.

Global top 12 lubricant manufacturers [162].

Manufacturers/Product Name	**Country**
Shell	Great Britain/The Netherlands
Exxon Mobil	USA
BP	UK
Chevron	USA
Petro China	China
Lukoil	Russia
Fuchs	Germany
Nippon Oil	Japan
Valvoline	USA
Conoco Philips	USA
Repsol	Spain
Indian Oil	India

2.8.3. Indian scenario of lubricant

In India, this type of work has been conducted at Indian Institute of Petroleum Dehradun [120]. Indian Oil Corporation Faridabad, Indian institute of chemical technology Hyderabad, Defense Materials and Stores Research and Development Establishment, Kanpur, Bharat Petroleum Corporation Limited and Hindustan Petroleum Corporation Limited, India.

In India, 100 million tons per annum of petroleum products are expected to be consumed in which lubricant consumption leads to 2 million tons per annum approximately. There is large-scale use of two and three wheelers in India which makes a lot of differences from that in the developed world. Among the lubricant consumption, engine oil is the most important base stock in which 97 % were obtained from petroleum crude oil and only 3 % from synthetic oil due to the cost consideration [119, 133]. Due to the emission legislation, the vehicle manufacturers are under pressure to reduce the emission of HC, CO,

NO_x and improve the air quality. Non-edible vegetable-based lubricants are potential candidates to meet environmental concern. There is increase in demand for the lubricants due to the ongoing expansion of vehicle manufacturers and other industrial activities due to the rapid industrialization and the increase in the trend of vehicle ownership.

2.9. Summary obtained from literature review

Non-edible vegetable oil-based bio-lubricants are biodegradable and renewable. In the case of automotive applications, the biodegradability of bio-lubricants is the strongest point. Automobile fuels and lubricants provide a plausible solution in obtaining renewable and eco-friendly lubricants because of environmental concern. Non-edible vegetable oils are environmentally compatible in comparison to petroleum-based mineral oils. However, there is a need to provide broader aspects of the market segment. Due to the environmental concern and the restrictions on environmental regulations, the use of lubricants in areas such as forestry, chain saw, and two-stroke engines are steadily increasing.

Non-edible vegetable oil-based bio-lubricants are the potential candidate for automotive applications. They have certain inherent technical properties which are better than mineral oils like high lubricity, viscosity, good anti-wear property, high viscosity index, high ignition temperature, increased equipment service life, high load carrying ability, excellent coefficient of friction, low evaporation rates, low emission of metal traces into the atmosphere and rapid biodegradability.

Still, they have not yet replaced petro based lubricants due to their inappropriate chemical structure, which lags them behind at various odd conditions during applications. The challenges in this field are to improve certain characteristics of vegetable oils without impairing their excellent tribological and environmentally relevant properties. Chemical modification of vegetable oils overcomes the structural problems related to vegetable oils which in turn make them fit for the application of lubricant. An increasing number of studies directed towards edible vegetable oil-based lubricants have been conducted but there is scanty of the literature in case of non-edible vegetable oil-based bio-lubricants. So, there is a need to focus on this area and finding out

some solutions related to the problems on the application of non-edible oils as bio-lubricant. Further, systematic research that affirms the tribological behavior of different bio-lubricant blends must be conducted. The present study can support as well as encourage research on using renewable non-edible oil-based bio-lubricants as alternatives.

CHAPTER 3

MATERIALS AND METHODS

The brief details of the methodology on the credibility of the jatropha and pongamia oil-based bio-lubricant are mentioned in Fig. 3.1. The entire study includes following steps: (i) Development and utilization of the developed jatropha and pongamia oil-based bio-lubricant (ii) Performance of the tribological characteristics (iii) Optimization of the operating parameters and development of the model (iv) The correlation of the operating parameters tested on a pin on disc (POD) tribometer with the diesel engine performance parameters with respect to the wear of the piston ring during the tribological analysis. The current study is aimed at the utilization of the pongamia and jatropha oil based bio-lubricant in comparison to the mineral oil and the detailed discussions are mentioned in the upcoming sections.

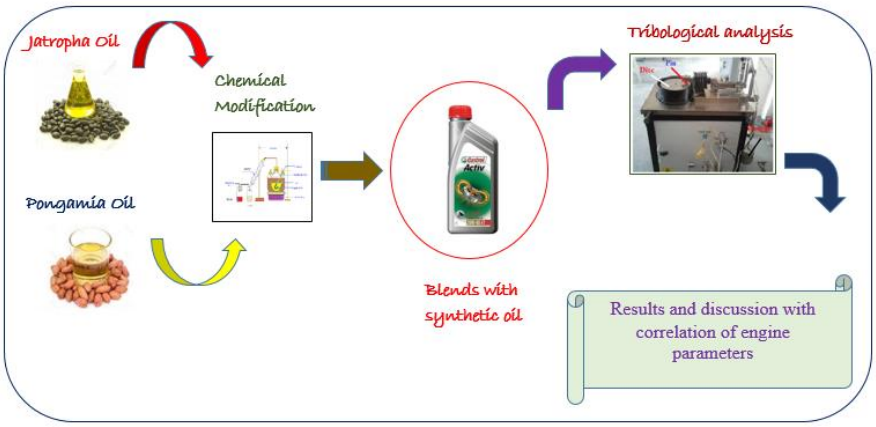
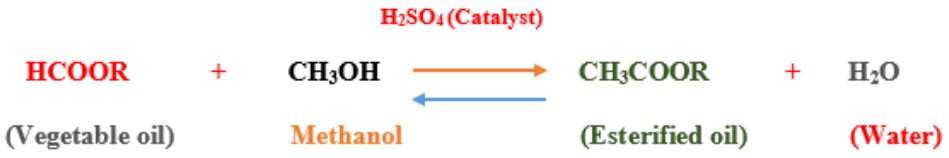


Figure 3.1. Schematic image of the processes included in the analysis.

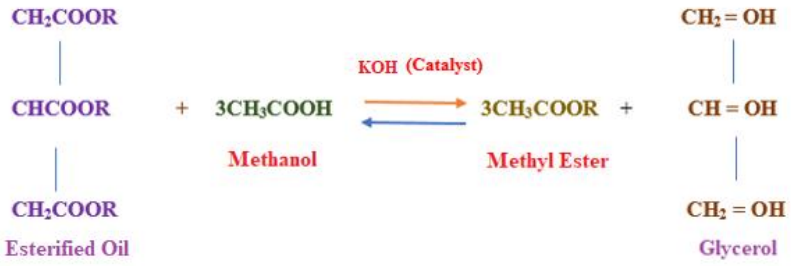
3.1. Development of the chemically modified bio based lubricant

For the production of bio-lubricant, crude pongamia and jatropha oil was collected from the New Delhi, India local market. The crude oil purchased contains a higher amount of free fatty acid as reported by Nitiema-Yefanova et al. [163] which needs to reduce below 1%. The Energy and biofuels Laboratory, Department of Mechanical Engineering, University of Petroleum and Energy Studies, Dehradun, India was used for the production of bio-based lubricant. The same process for the production of bio-lubricant was followed as mentioned

in the literature [111]. To make the pongamia and jatropha oil suitable for the tribological application, chemical modification or transeterification process is needed for the improvement of the properties of the oil. Two-step acid-base transesterification process was applied consisting of esterification and transesterification processes for reducing the free fatty acid amount as shown in Fig 3.2. During the esterification process, crude pongamia and jatropha oil were mixed with methanol in the ratio of 20:1 in the presence of sulphuric acid in the amount of 0.5% (w/w) as a catalyst. Further, transesterification process was applied to the Tran-esterified jatropha and pongamia oil obtained during the first step of the reaction. They mixed with methanol in the ratio of 6:1 by using sodium hydroxide as a catalyst with the presence of 1% (w/w). The methyl ester was produced with the presence of the glycerol which was separated with the help of filter after keeping the solution for a day so that separation in the layers of methyl esters and glycerol happened. The obtained methyl ester was further processed to modify its properties and make it as a suitable bio-lubricant for the tribological application. The jatopha and pongamia methyl esters were mixed with trimethylolpropane in the presence of 1% sodium methoxide ($NaOCH_3$) for obtaining modified oil with the help of the reaction shown in Fig 3.3. The chemical reaction for the preparation of the methyl esters was performed in a three-neck flask connected with the condenser as shown in Fig 3.5. The obtained oil was poured from the flask as early as possible to prevent the reversible reactions occurs during the process. The three-neck flask was kept in then oil bath while maintaining the temperature around 120^{o}C. The process was conducted around 8 hours to get the desired output. At the last stage, modified pongamia and jatropha oil was separated by performing the filtration process using filter papers.



(i)



(ii)

Figure 3.2. Details of the process used for the two-step transesterification process.

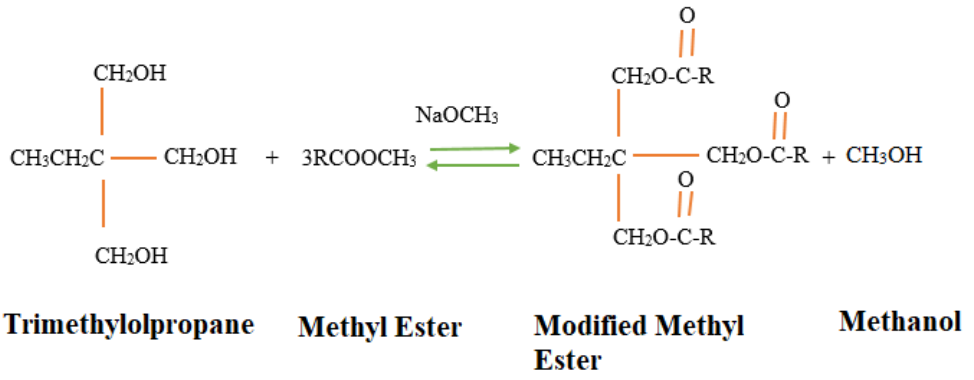


Figure 3.3. Process applied for the chemical modification of the obtained methyl ester.

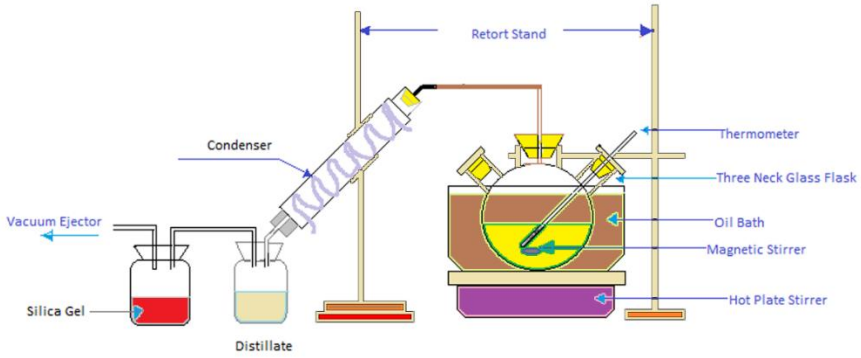


Figure 3.4. Chemical modification experimental set up schematic image [164].

3.2. Process applied for the preparation of bio-lubricant samples

For the further processing of the addition of the chemical modified bio-based lubricant to the mineral oil (SAE20W40), mineral oil was purchased from the M/s R S Lubricants, Dehradun City, Uttarakhand. The SAE20W40 mineral was used for the lubrication purpose in vehicles and it is easily available in the local market. Seven types of samples were prepared for the test in which six samples consists of a blending of modified bio-lubricant with the mineral oil. The blending was performed in the following ratios: 5%, 10% and 15%. The percentages include the volume of bio-lubricant added to the mineral oil. The samples are designated as M100, PB5, PB10, PB15, JB5, JB10, and JB15 consisting of pure mineral oil and bio-lubricant with added to the mineral oil with different proportions. The addition of the reference oil to the bio-lubricant was performed using a magnetic stirrer. To avoid the phase separation and stability of the blends, Diesterol was used as the surfactant. The mineral oil in a certain quantity was mixed with the bio-lubricant in a flask and the solution was placed on the stirrer for the further process of blending. The temperature of the stirrer was maintained at 65^{o}C temperature and 700 rpm rotating speed. The process was conducted for around 2 hours for each samples and further ultrasonication process was done. The ultrasonication was done for around 15 minutes under the influence of ethanol bath at a temperature of 65^{o}C. The dynamic light scattering technique was used to check the quality of the blending of mineral oil to the bio-lubricant. The samples are illuminated by laser to study the speckle pattern.

3.3. Physicochemical properties of the bio-lubricant

Evaluation of the properties was necessary for the determination of the characteristics of the oil. Kinematic viscosity, viscosity index, density, flash point, and acid value were measured according to the following ASTM standards: ASTM D445, ASTM 2270, ASTM D93, ASTM D664 respectively. Table 3.1 shows the properties of the samples considered for the tribological analysis. Kinematic viscosity at 40^{o}C and 100^{o}C were determined using Stabinger viscometer, SVM 3000 model (Anton Parr, UK). The samples used for the analysis may contain a certain amount of the acidic value which needs

to be determined as it leads to the degradation of the lubricant if available in a significant amount. The acid number can be determined by using the titration process by utilizing KOH as the titration agent. The KOH was added to the isopropanol in the amount of 0.2 mol/l. The range of acid numbers included in the precision statement was 0.1 mg/g KOH to 150 mg/g KOH. Density was measured at 15^{o}C using a pycnometer based on weight to the volume ratio. Closed cup tester (Pensky-Martens PMA4) was used for the measurement of the flash point. All the tests were performed three times and the average value was reported.

Table 3.1.

Physicochemical properties of the samples used for the tribological analysis.

S. No.	**Properties**	**M100**	**JB5**	**PB5**	**JB10**	**PB10**	**JB15**	**PB15**
1.	Kinematic viscosity (cST) @ 40^{o}C	148 .3	112.4	119.4	122.3	126.1	150.2	152.3
2.	Kinematic viscosity (cST) @ 100^{o}C	15.2	12.2	12.8	13.6	13.9	15.9	16.4
2.	Flash point, °C	272	228	235	244	251	259	265
3.	Total acid number (mg KOH/g)	0.44	0.48	0.50	0.54	0.59	0.65	0.68

4.	Density (gm/cm^3) @ 15^oC	0.9412	0.9231	0.9249	0.9312	0.9358	0.9522	0.9568

Table 3.2.

List of the equipment's and standard methods followed.

Test performed	**Standard method**	**Name of the equipment**	**Manufacturer details**	**Model**	**Accuracy**
Viscosity at 40^oC (cSt)	ASTM D 445	Stabinger viscometer	Anton parr	SVM 3000	± 0.1 cSt
Viscosity at 100^oC (cSt)	ASTM D 445	Stabinger viscometer	Anton parr	SVM 3000	± 0.1 cSt
Friction and wear	ASTM G99	Pin on disc machine	DUCOM	TR20LE	-
Wear scar diameter	ASTM 4172	Optical microscope equipped with view 7 software	Nikon Eclipse	LV150	± 0.1 mm
Worn surface	X30/X2000	Scanning electron microscope	Jeol	JSM5200	-
TAN	ASTM D664	Automatic Titrator	LabIndia	-	-
Oil degradation	ASTM D4628	Flame atomic absorption	Perkin Elmer	PinAAcle 900z	± 0.01 Abs

spectromet
er

3.4. Friction and wear analysis

3.4.1. Pin on disc tribometer

For the tribological analysis of the selected lubricants, Pin-on-Disc Wear tester TR-20LE supplied by the DUCOM, India was used. The schematic image of the experimental set up is shown in Fig. 3.5. The POD machine was connected to the computer equipped with a data acquisition system. It was inbuilt with software for the assessment of the frictional force, coefficient of friction, and wear rate at different operating conditions. An oil tank with a capacity of 3 litre was connected consisting of a hydraulic pump having a supply mode for the constant supply to the testing surface. The disc was rotated around the centre of the disc with the help of DC servomotor and sliding speed was controlled with the help of the controller attached through feeding the desired value in the system. The detailed specifications of the Pin-on-Disc wear tester is mentioned in Table 3.3.

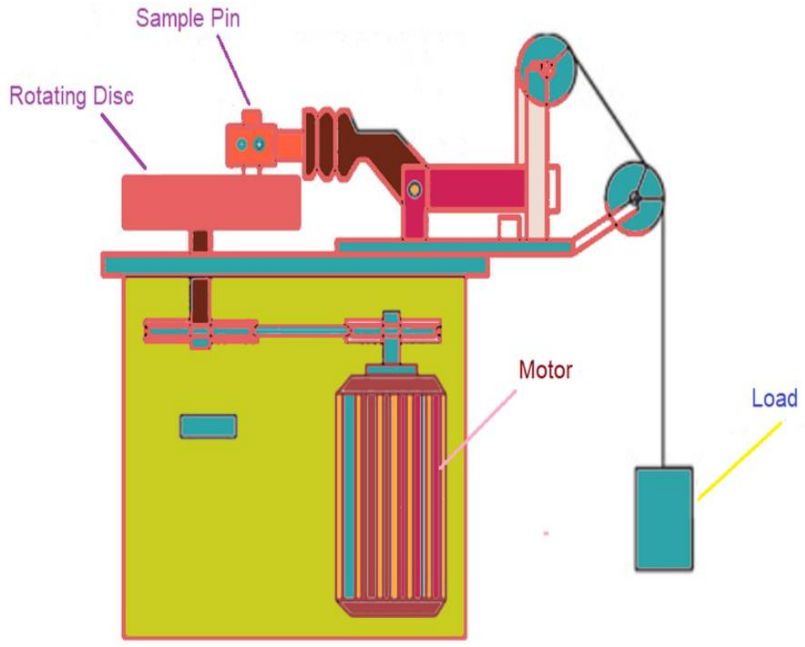


Figure. 3.5. Schematic image of the pin-on-disc experimental set up.

Table 3.3.

Specifications of the POD machine.

Parameters	Min	Max
Diameter of the pin, mm	3	12
Diameter of the disc, mm		165
Rotating speed of the disc, rpm	200	2000
Applied load, N	1	200
Frictional force, N	1	200
Wear measurement range, μm	1	1200
Range of temperature, ^{o}C	1	300
Wear track diameter, mm	50	145

3.4.2. Parameters considered for the analysis on POD tribometer

The details are: applied load/contact pressure = 40 to 200 N /31.8 to 159.2 x 10^5 N/m^2; temperature = 150^{o}C; track diameter = 80 mm (for each conditions); sliding speed/velocity= 300 to 1200 rpm/1.3 to 6.3 m/s; sliding distance= 30000 m. The same track diameter and the sliding distance were considered for each test performed on the pin on disc machine. The pin was held stationary during the process of the analysis by rotating the disc at the desired speed by loading the arm with selected loads. The friction track was equipped with the sensors for obtaining the friction values. For the proper cleaning and making disc suitable for the test, A350 emery paper was used for polishing them before and after conducting each experiment. Before the examination of the surface of the pin, it was cleaned in an ultrasonic bath in the presence of acetone maintaining a temperature of 65^{o}C. After the cleaning process, a pin was placed in the desiccator to get it dry to avoid its contact with atmospheric dust available

for a better examination of its surface. The pin was weighted using a weighing balance machine having an accuracy of around ±0.001 gm. The temperature was applied with help of an isolated chamber after keeping it on the pin on disc contact surface and the value was fed to the controller equipped with the set up for the possible temperature range.

3.5. Oiling concept

A single fused silica capillary tube consisting of an outer diameter of 370 µm and an inner diameter of 210 µm was used for the supply of the oil to the surfaces in contact. The capillary tube was capable to be bent as per the requirement of the surfaces in contact for proper flow during the process implemented. The bending of the capillaries was maintained at 3 mm from the surfaces in contact so that the proper formation of the lubricant layer can be obtained. The oil flow rate can be varied with a high precision range from 0.001 ml/min to 10 ml/min. Around 5 ml/min flow rate was maintained while conducting each test for determining tribological analysis.

3.6. Experimental procedure

The experiment was conducted on POD tribometer to evaluate the effect of the different lubricants used for the analysis. The material of the pin was obtained from the piston ring of the engine and it was fixed in the specially designed pin holder so that it can maintain a sliding contact to the surface of the disc. The dimensions of the pin were 30 mm in length and 8 mm in diameter with a spherical shape from the front side. The disc was obtained from the M/s Agrawal metal works, Roorkee City, Uttarakhand by using the melting and machining process applied for obtaining the desired shape of the disc. The piece of the pin was small in size so, it was fitted in the grooves of another plate having desired dimensions. The weight of the pin was measured on an electric weighing machine (10^{-4} g sensitive scale) and wear was plotted as per the difference obtained at operating conditions. Specific wear rate was obtained according to the Archard's equation:

$$W_s = \frac{V}{L * F_n} \qquad (3.1)$$

Where, W_s is the specific wear rate (mm^3/Nm), V is the volume loss (mm^3), L is the sliding distance (m) and F_n is the normal applied load (N).

Volume loss was obtained as per the ASTM standards. The lower part of the pin was spherical in shape having a curvature radius of 4 mm.

$$V = \frac{\pi(WSD)^4}{64*r} \quad (3.2)$$

Where, V is the volume loss in mm^3, WSD is the wear scar diameter in mm and r is the radius of the spherical pin in mm.

After conducting each experiment at desired operating conditions, wear scar diameter was measured using an optical microscope with a resolution of 0.01 mm (ASTM D4172) equipped with view 7 software. The lower part of the pin was held on the platform of the microscope in a position of facing its scar upward towards the microscope lens. The microscope lens was adjusted and focused to get a clear image of the scar obtained on the surface of the pin. After detecting the scar, the image was captured and saved in the system by pressing the capture button provided. With the assistance of the software, wear scar diameter was measured in mm range with the help of the scale inbuilt to the view 7 software. SEM analysis was conducted to check the wear on the surface of the pin with a magnification capacity of 500x.

3.7. Diesel engine experimental setup

The schematic image of the engine is shown in Figure 3.6. This test engine has been supplied by Kirloskar Ltd. The engine is connected to a computer employed with engine software designed by Legion brother's agency. Initially, the engine was run on a neat diesel around 20 minutes before changing the mode of the lubricant supplied until the temperature of the lubricant reaches to around 80^oC to maintain a steady state condition.

Table 3.4 represents the technical specifications of the engine. The test on the engine is was performed at the operating conditions set by suppliers during its usage. It includes injection timing of 23^obTDC (before top dead centre) and 18MPa fuel injection pressure.

Table 3.4.

Diesel engine specifications

Make	**Kirloskar**

Type	4S, DI diesel engine
Bore and Stroke, mm	87.6 and 110 respectively
Capacity, Litre	0.661
Compression ratio	17.5:1
Loading	Eddy current dynamometer (water cooled)
Rated power	5.2 kW at 1500 rpm
Crank angle sensor	Resolution 1°, speed 5500 rpm with TDC pulse
Inlet valve open, °bTDC	4.5
Inlet valve closed, °aBDC	35.5
Exhaust valve open, °bBDC	35.5
Exhaust valve closed, °aTDC	4.5
Fuel injection timing, °bTDC	23
Fuel injection pressure, MPa	18
Starting	Manual cranking
Lubrication	Forced

The experimental observation was taken three times and the average value was considered for the evaluation. The engine responses like BTE, BSFC, etc was obtained with the help of the Legion brother's engine data acquisition software. The AVL Di 444-gas analyser was used for the emission analysis. The technical specification, accuracy and percentage of the uncertainty of the UHC exhaust engine response are mentioned in Table 3.5. The UHC emission was considered to clarify the details obtained during the emission analysis while considering uncertainties.

Table 3.5.

Technical specifications and accuracy of the AVL Di Gas 444 gas analyser.

Measurement	Range of instrument	Accuracy achieved	% uncertainty
UHC	0-20,000 ppm Vol	<200 ppm volume ±1 ppm volume >200 ppm % Vol: ±1%	±0.2
Warm up time	10 min. (self-controlled) at 25°C operating temperature		
Response time	Within 10 seconds for 90 % instrument response		

Top piston ring of the piston was weighed before and after the performance of each experiment. The wear in gm was calculated by taking the difference in the weight of the top piston ring before and after conducting each experiment as per the matrix generated using the RSM technique. The running test duration of the engine was 125 hour.

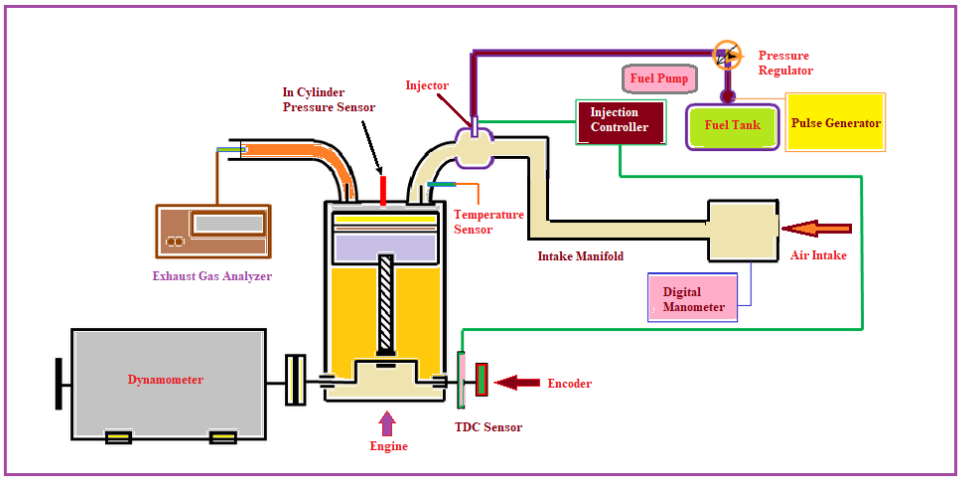


Figure 3.6. Schematic image of the diesel engine set up.

3.8. Error analysis

Error analysis was important to check the uncertainty level in the reproductive results. The test was performed repetitively three times and the uncertainty level was checked according to the linearized approximation

method of calculation. A sample calculation has been provided in Appendix A. The uncertainty level was below ±5% error and the polynomial trend line curve was well fitted for the presentation and discussion of the results obtained. The calculated relative uncertainty level of different parameters including COF, SWR, WSD, wear has been mentioned in Table 3.5.

Table 3.6.

The uncertainty level of the parameters.

Parameter	Level of accuracy	Level of uncertainty
COF	±0.5	±1.23
SWR	±0.5	±2.78
WSD	±0.01 mm	±1.75
Wear	±0.005 gm	±1.39

3.9. Correlation of the parameters using response surface methodology

To correlate the parameters considered during the POD tribometer test with the engine, the experiment was designed and performed using RSM optimization technique [59]. The input parameters considered during the study were lubricants, load and sliding speed and the response parameters were wear obtained from the POD tribometer and the engine.

The objectives of this study are: (i) to enumerate the main and interactive effects of the input parameters with the response parameters (ii) development of the regression models for the wear obtained at both pin on disc apparatus and the engine using the full factorial design that can accurately describe the experimental data, and (iii) to obtain an optimum combination of the considered factors to minimize the wear during the conditions adopted with maximum possible efficiency using the desirability approach.

3.9.1. Design of experiments (DOE)

Theoretical predictions based on experimental observations mark the essence of useful research. Proper use of statistical methods greatly improves the efficiency of the experiments and helps to draw meaningful conclusions from the experimental data. There are two basic aspects of concern in scientific experimentation: the design of the experiment and the statistical analysis of the data. Successful experimentation requires knowledge of the important factors

that influence the output. The design of experiment (DOE) [165] helps to determine the factors, which are important for explaining a process variation. Interactions are the driving forces in many processes and proper understanding of the process may be difficult or impossible if important interactions remain undetected. DOE also helps to understand how the influential factors interact with the system. Methods such as factorial design, response surface method (RSM) and Taguchi techniques can be used for planning the experiments. In the present paper, RSM is used for studying the influence of input parameters on the response parameters.

In general, the typical input parameters of interest while evaluating the tribological properties are load, speed, and concentration of lubricant. These parameters have been taken based on the review of literature, experience and discussions [41, 166-171]. From the introductory investigation, it is noted that the linear model is insignificant due to the chaotic behaviour of the responses; therefore a second order model is necessary for analyzing the effect of the test parameters on the performance measures of the lubricants.

The input parameters like lubricants, loads and sliding speed are having a considerable impact on the output responses including the wear while utilizing POD machine and the engine. However, to check the utility of a particular parameter on the wear of the samples takes a certain amount of time as there is a lot of combinations required between the input parameters applied during their tribological analysis. Therefore, optimization of the process parameters is a significant way by which the time utilized during their analysis can be reduced. The RSM technique can be applied to the process parameters without any break during its process as it reduces the number of experiments and also provides an optimum combination of the process parameters applied for getting improved results [59, 172-175].

There are various designs available during the application of RSM technique in which Box-Behnken design is one of them. This design is only applicable to the continuous factors considered in an odd range up to a limit of 13. This design was applied to consider the impact of individual and interactions of input parameters on the wear of the surface. Table 3.7 shows

the levels of the input parameters considered for the study with coded values. The levels with their range was designated as I_{imin}, minimum value, I_{imid}, mid-range value, and I_{imax}, maximum value for every parameter which corresponds to -1, 0 and +1 levels, respectively. The equation used for the process was mentioned as follows:

$$I_i = \frac{2(I_{actual} - \bar{I})}{(I_{imax} - I_{imin})} \quad (3.3)$$

Where, $I_i = \frac{I_{imax} - I_{imin}}{2}$

Table 3.7.

Operating conditions and their experimental levels.

Operating parameters	**Level – 1**	**Level-2**	**Level-3**
Sliding speed (A)	-1 (900)	0 (1200)	1 (1500)
Load (B)	-1 (100 N, 50 %)	0 (150 N, 75 %)	1 (200 N, 100%)
Lubricant (c)	-1 (0)	0 (5)	1 (10)

3.9.2. Desirability approach

A detailed description of this approach can be found in the literature. [16, 176, 177]. The desirability approach was applied to check the validation of

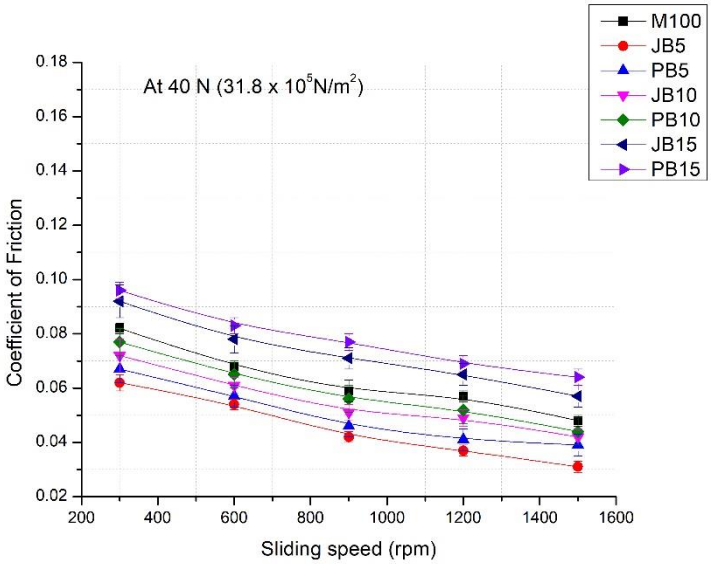
the model generated during the regression analysis. This approach results in a productive combination of the input parameters with an optimum result of the response parameters considered. The criterion of this investigation is to minimize the wear which is an effective way for the improvement of the engine performance.

CHAPTER 4
RESULTS AND DISCUSSIONS

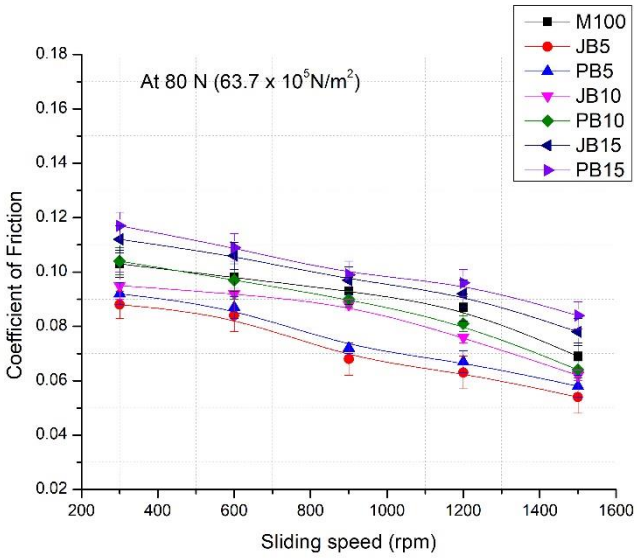
4.1. Coefficient of friction analysis

Friction force was produced due to the applied loads (contact pressure) exerted on the pin and the average value was obtained on the monitor of the setup during the tribological characterization.

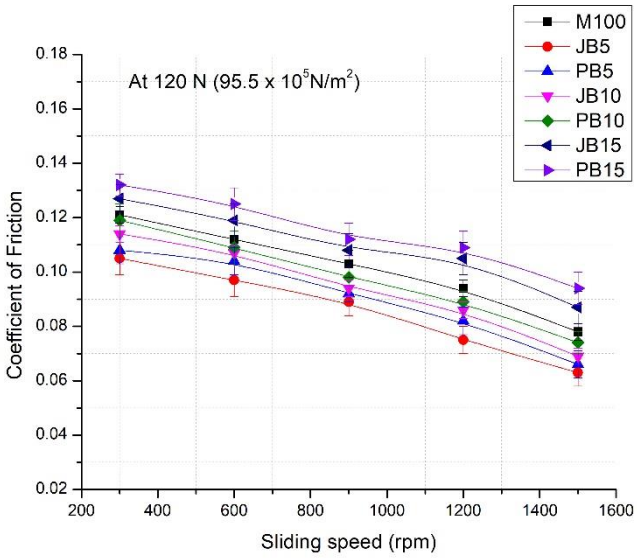
Figure 4.1 shows the coefficient of friction values obtained at different load with a variation of speed during the analysis. The sliding distance and the temperature were maintained constant during the test. With reference to the load, the maximum amount of coefficient of friction was obtained at a higher contact pressure or load and the minimum was observed at the lower load. The amount of coefficient of friction varied based on the applied pressure. With an increase in the applied pressure, the stress on the surfaces in contact results in more amount of coefficient of friction [178]. The coefficient of friction was varied ranging from 0.03 to 0.17 during load as the pressure increases with an increase in load. Minimum coefficient of friction was observed at 5 % and 10 % lubricant blends and the maximum was obtained at 15 % blends. The minimum range of coefficient of friction was observed at 40 N load and maximum obtained at 200 N load which ranges from 0.06 to 0.09 and 0.12 to 0.18 respectively.



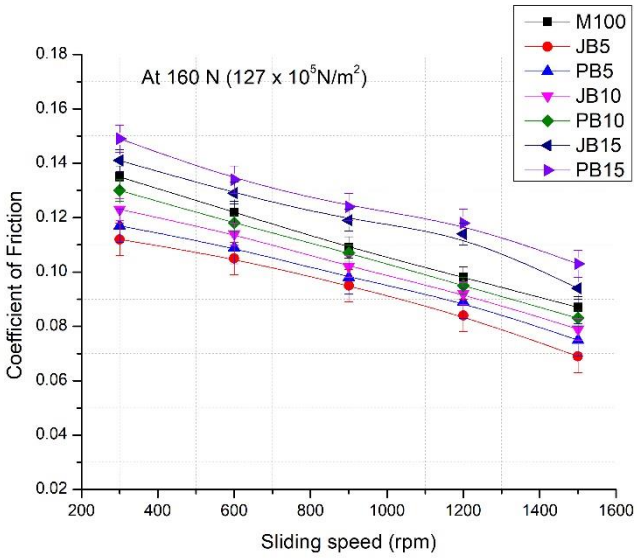
(a)


At 80 N (63.7 x 10^5N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Coefficient of Friction
Sliding speed (rpm)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
200
400
600
800
1000
1200
1400
1600

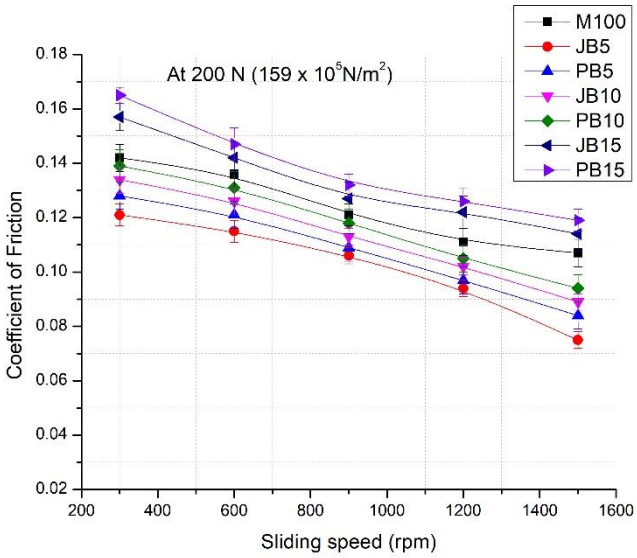
(b)


At 120 N (95.5 x 10^5N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Coefficient of Friction
Sliding speed (rpm)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
200
400
600
800
1000
1200
1400
1600

(c)



(d)

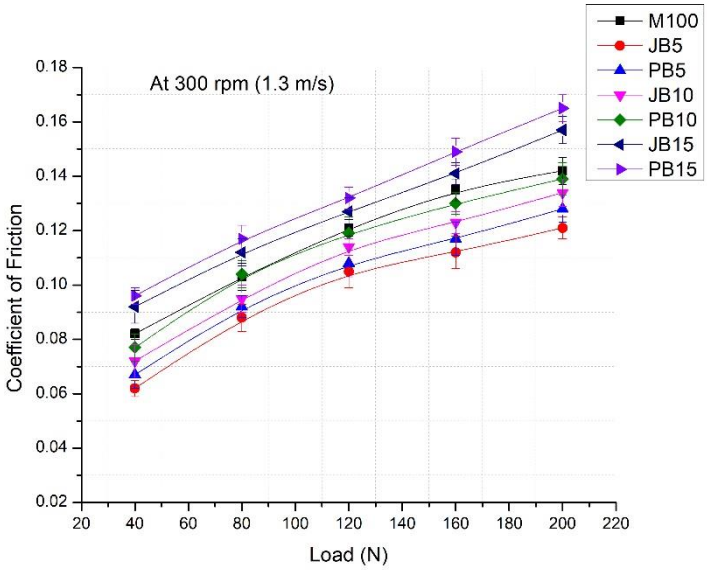


(e)

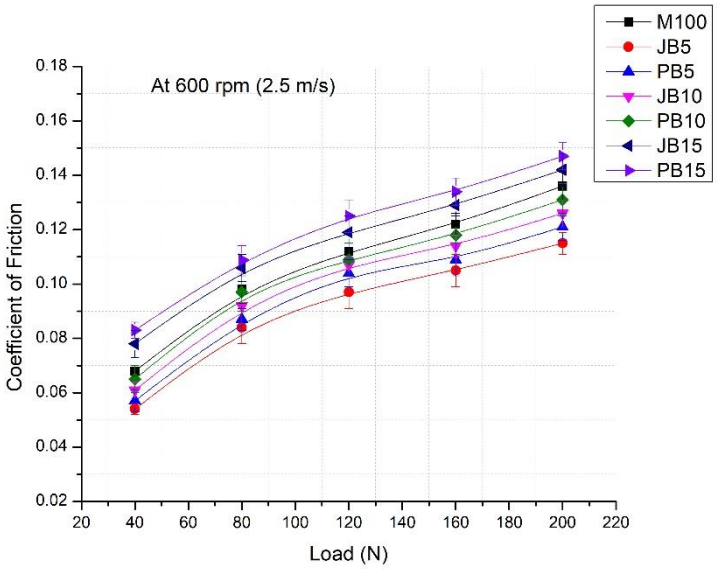
Figure 4.1. Coefficient of friction with variation of speed during different load (a) 40 N (b) 80 N (c) 120 N (d) 160 N (e) 200 N.

Fig 4.2 shows the variation of sliding speed with the coefficient of friction. The coefficient of friction with respect to the sliding speed decreases with an increment in its value. The coefficient of friction value varied from 0.03 to 0.17 and the maximum disparity in the coefficient of friction was obtained at a lower speed with respect to the higher speed. With an increase in sliding speed,

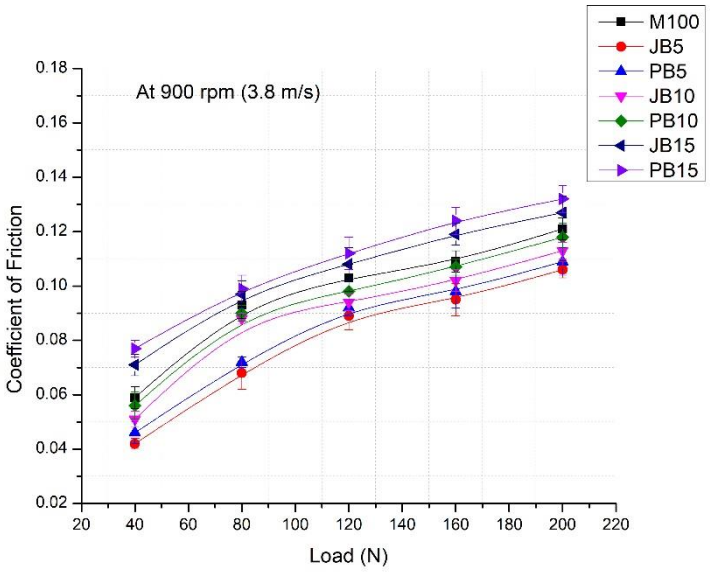
the surfaces in contact don’t obtain the desired time for their proper interaction with the applied loads which results in a decrement of the coefficient of friction [66].



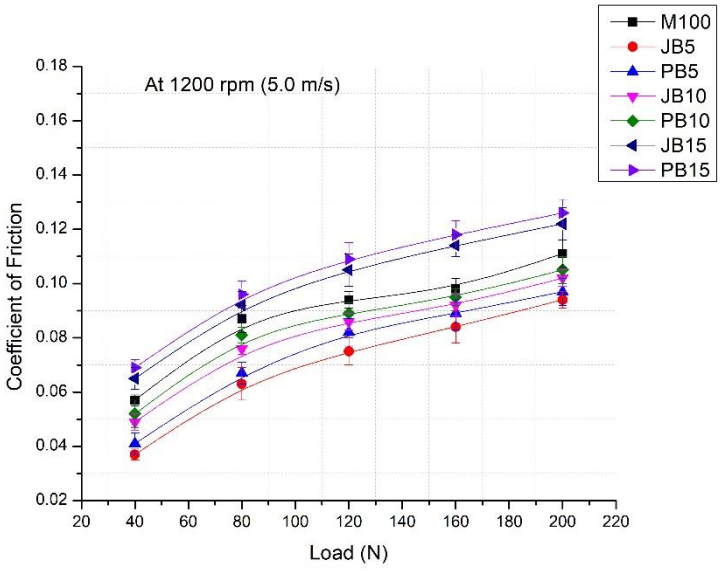
(a)



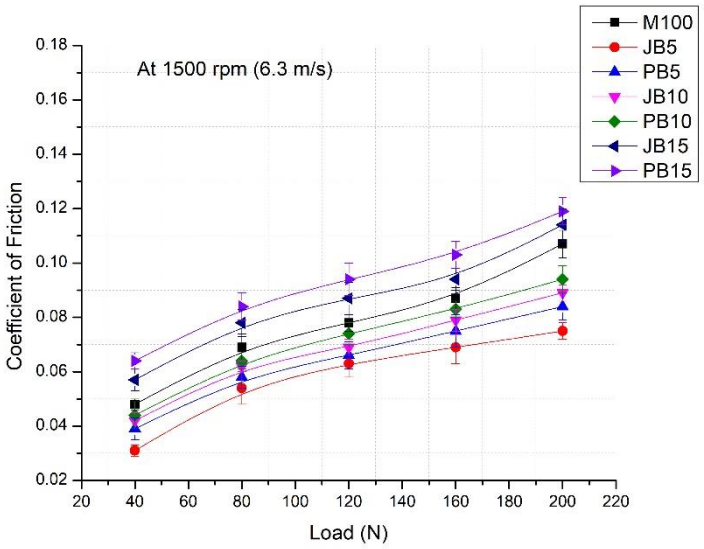
(b)


At 900 rpm (3.8 m/s)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Coefficient of Friction
Load (N)
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
20
40
60
80
100
120
140
160
180
200
220

(c)


At 1200 rpm (5.0 m/s)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Coefficient of Friction
Load (N)
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
20
40
60
80
100
120
140
160
180
200
220

(d)



(e)

Figure 4.2. Coefficient of friction with different loads at various sliding speed or velocity (a) 300 rpm (b) 600 rpm (c) 900 rpm (d) 1200 rpm (e) 1500 rpm.

The boundary lubrication conditions are obtained during the conditions stated earlier based on the Stribeck theory, COF significantly decreases while increasing the sliding speed [179, 180]. There is an increment in the hydrodynamic proportion of the lubricants which results in the decrement of the COF while increasing the sliding speed.

The influence of the bio-based lubricants during the conditions applied above is more in comparison to the certain parameters like load, sliding speed, temperature, and sliding speed. They are sustainable in forming a lubricant film between the surfaces during their sliding contact. While considering the effect of different lubricant samples, the amount of coefficient of friction shows the minimum value at 5 % and 10% blends of bio-lubricant with reference to the mineral oil. The 15% blending of bio-lubricant shows the maximum coefficient of friction with respect to the mineral oil. More than 10% decrement in the value of the coefficient of friction was observed at a 5% blend with respect to the mineral oil. This trend is observed for all the conditions applied during their analysis. The decrease in the coefficient of friction depends upon the capacity of the sustainability of the lubricant film between the surfaces in contact. The

formation of the long molecular chains and the branches of the bio-lubricant contribute to the reduction of the coefficient of friction. The long-chain fatty acid components resulted in the formation of a multi and mono-layer on the sliding surfaces during their contact which reduces the effect of forces generated while the load is applied [152].

The polarity in the structure of the non-edible oils also presents a significant role during their tribological analysis. The formation of the thin lubricant film occurs between the surfaces in contact based on the absorption of the polar compounds which was based on the chemical reaction occur on the surface during their characterization. The extent of oleic acid in the non-edible oils also contributes to deciding the amount of coefficient of friction obtained. The chemically modified jatropha oil contains a higher amount of oleic acid in their structure with respect to the chemically modified pongamia oil which results in more reduction in COF value during their comparison analysis with respect to the reference oil.

The presence of fatty acids and their effectiveness to provide a better lubricity is well known in the literature [181, 182]. The presence of more amount of polarity in the fatty acids compositions of non-edible oils results in the development of a protective film which was occurred when carboxyl group (COOH) was attracted more to the surfaces during their sliding contact [136]. Therefore, there is a significant reduction in the amount of coefficient of friction was observed while using a bio-based lubricant with comparison to the mineral oil. The maximum COF was shown by the 15 % blends which were due to the dilution of the blends and resulted in the weak form of the protective film between the sliding contacts as compared to the other blends. The viscosity also plays a vital role while forming a protective layer between the surfaces in contact. The higher viscosity results in the resistance to the flow of the fluid and the wear of the elements from the surface don’t flow in a proper way which prevents the proper interaction the surfaces during their sliding contact. The 15% blends show higher viscosity results in more amount of coefficient of friction with respect to the mineral oil [183].

The compositions of the saturated and unsaturated fatty acids in the non-edible oils provide a significant influence on the coefficient of friction characterization. The gas chromatography was a significant analysis while determining the amount of compositions of fatty acids contained in the non-edible oils. The vegetable oils contain double bonds that resist their capacity to form a suitable lubricant film on the surface. To modify their structure and to reduce the unsaturation level, chemical modifications like epoxidation, transesterification, etc are better due to their short duration of time, high yield and least cost. The fatty acid composition of the oil was estimated according to the European standard method EN14103.

The fatty acid composition of oil was analyzed by a Gas Chromatography-Mass Spectroscopy (GC-MS) (GC-10, Shimadzu, Japan) equipment having a capillary column with 30 mm length and 0.25 mm diameter lined with a 0.25 μm (Rtx-5 ms, Rextex). Samples were injected in the split/column flow ratio 24:1. Helium was used as the carrier gas with a flow rate of 1 ml/min. The injection temperature and the oven temperature was maintained at 250 °C (programmed to start at 120 °C, held at this temperature for 5 min and heated at a rate of 3 °C/min to 250 °C). Figure 4.3. shows the fatty acid composition of the oils.

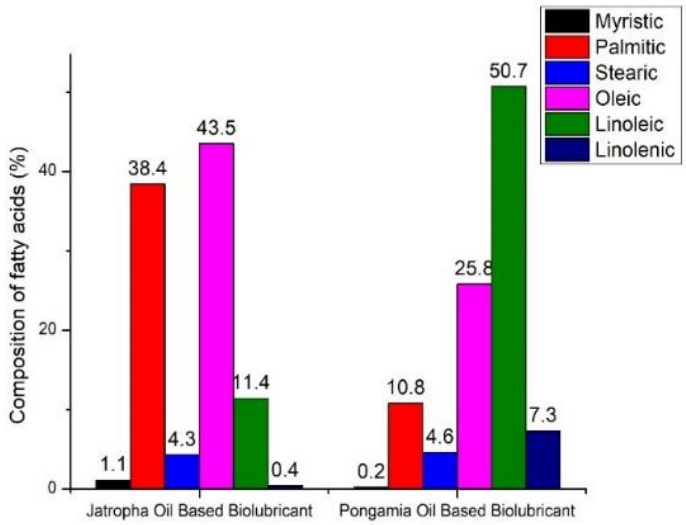


Figure 4.3. The fatty acids compositions for the chemically modified jatropha and pongamia oil samples considered in this study.

The presence of more amount of unsaturated fatty acids composition in the oil results in the increment of the coefficient of friction. The unsaturated fatty acids consist of more amount of linoleic and oleic acid which contributed more to the increment of COF with respect to the saturated fatty acids (stearic acid). The presence of the double bond in the saturated acids is almost negligible which results in the formation of a straight chain of the molecules resulting in a closely packed structure contributing to the development of a strong protective film between the surfaces in contact [184]. While on the other hand, unsaturated fatty acids consist of double bonds resulting in bending of the structure of the chain formed as shown in Figure 4.4. This will not result in the formation of a closely packed molecule structure on the surfaces during their contact. The presence of unsaturated fatty acids in the structure of pongamia oil is more in amount than the jatropha oil [52] which contributed towards the increment of the coefficient of friction between the surfaces in contact.

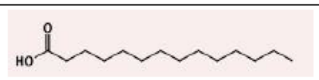
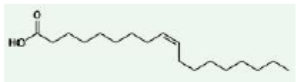
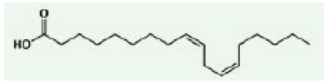
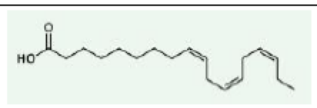
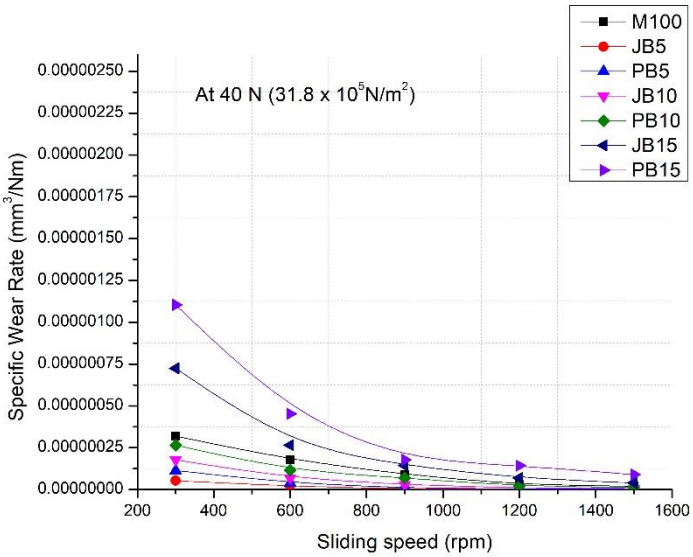
	Type of acid	Chemical structure
Saturated	Myristic ($C_{14}H_{28}O_2$)	
	Palmitic ($C_{16}H_{32}O_2$)	
	Stearic ($C_{18}H_{36}O_2$)	
Unsaturated	Oleic ($C_{18}H_{34}O_2$)	
	Linoleic ($C_{18}H_{32}O_2$)	
	Alpha Linolenic ($C_{18}H_{30}O_2$)	

Figure 4.4. Different types of fatty acids molecular structure [53].

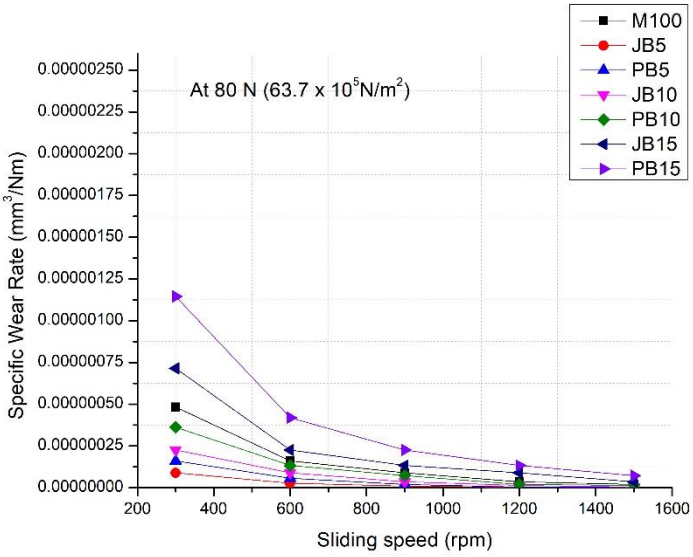
4.2. Wear analysis

The specific wear rate was compiled in Figures 4.5 and 4.6 with respect to the applied load or contact pressure and sliding speed (velocity). The 5 and 10 % addition of the jatropha and pongamia oil shows minimum wear compared to the conventional mineral oil for all applied conditions irrespective

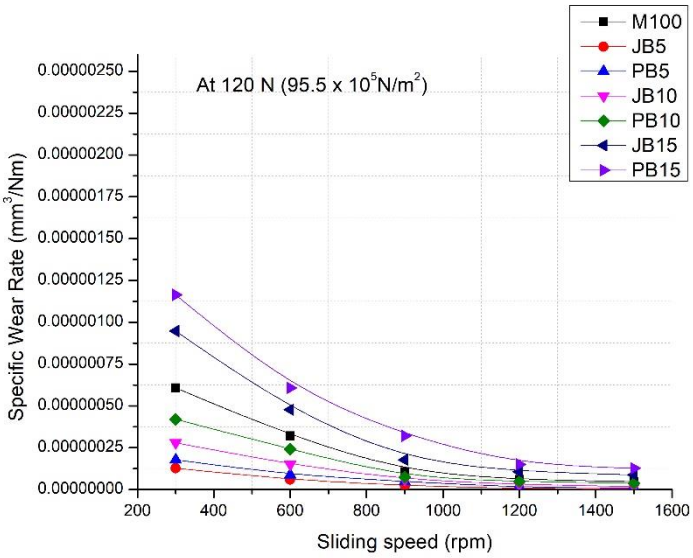
of the sliding distance. All the blends follow the same trend as mentioned in the earlier section of COF.



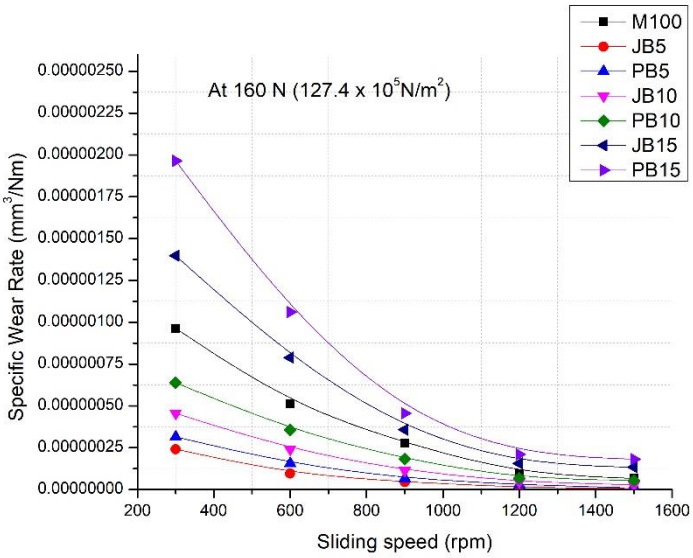
(a)



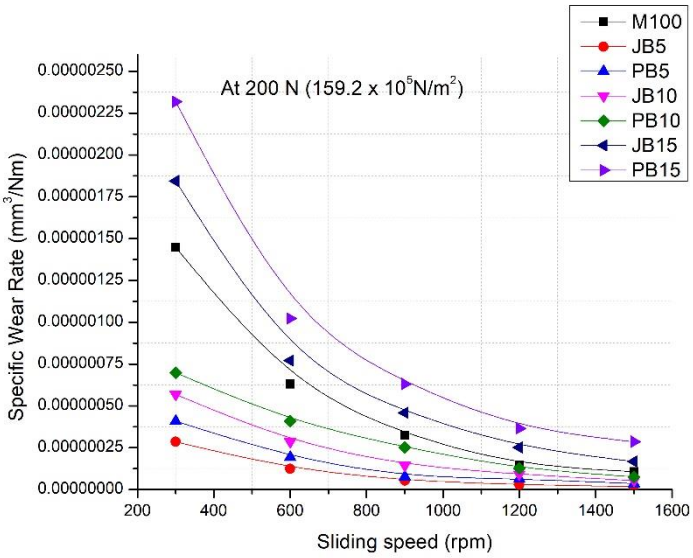
(b)


M100
JB5
PB5
JB10
PB10
JB15
PB15
At 120 N (95.5 x 10^5N/m^2)
Specific Wear Rate (mm^3/Nm)
0.00000250
0.00000225
0.00000200
0.00000175
0.00000150
0.00000125
0.00000100
0.00000075
0.00000050
0.00000025
0.00000000
200
400
600
800
1000
1200
1400
1600
Sliding speed (rpm)

(c)

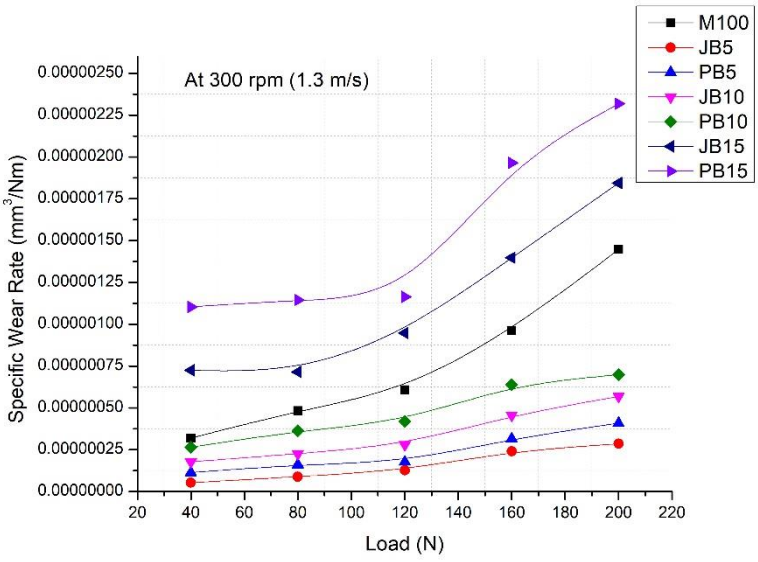

M100
JB5
PB5
JB10
PB10
JB15
PB15
At 160 N (127.4 x 10^5N/m^2)
Specific Wear Rate (mm^3/Nm)
0.00000250
0.00000225
0.00000200
0.00000175
0.00000150
0.00000125
0.00000100
0.00000075
0.00000050
0.00000025
0.00000000
200
400
600
800
1000
1200
1400
1600
Sliding speed (rpm)

(d)

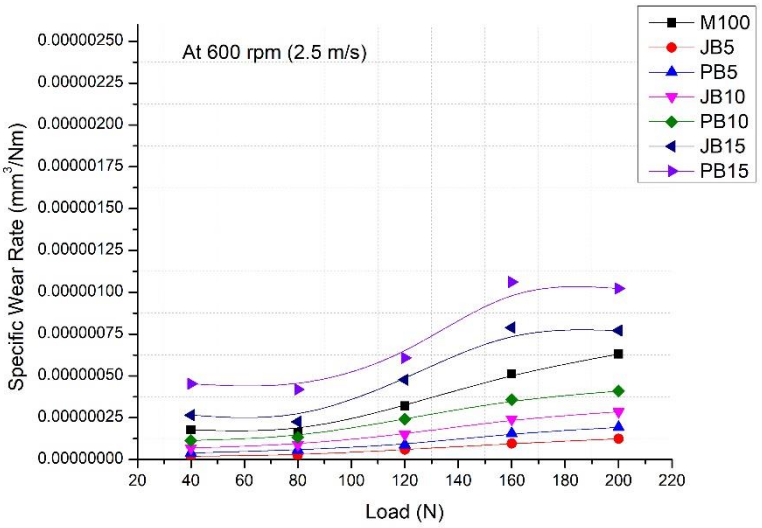


(e)

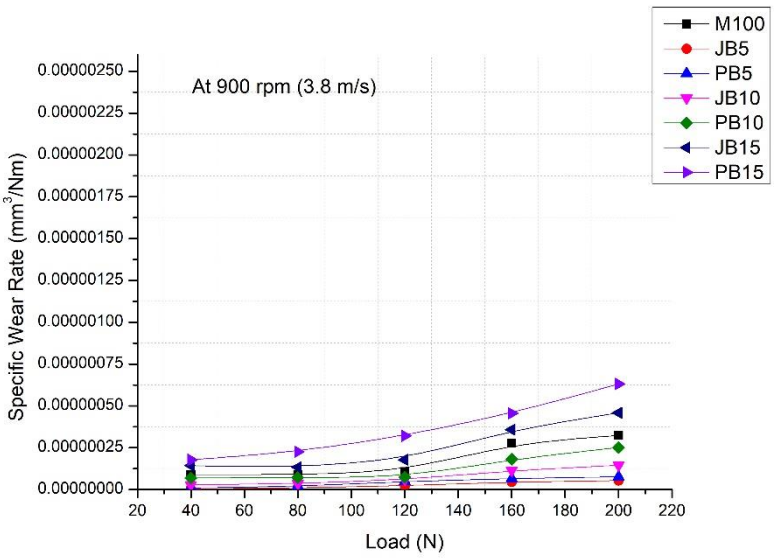
Figure 4.5. Specific wear rate with respect to speed at different load (or contact pressure) (a) 40 N (b) 80 N (c) 120 N (d) 160 N (e) 200 N.



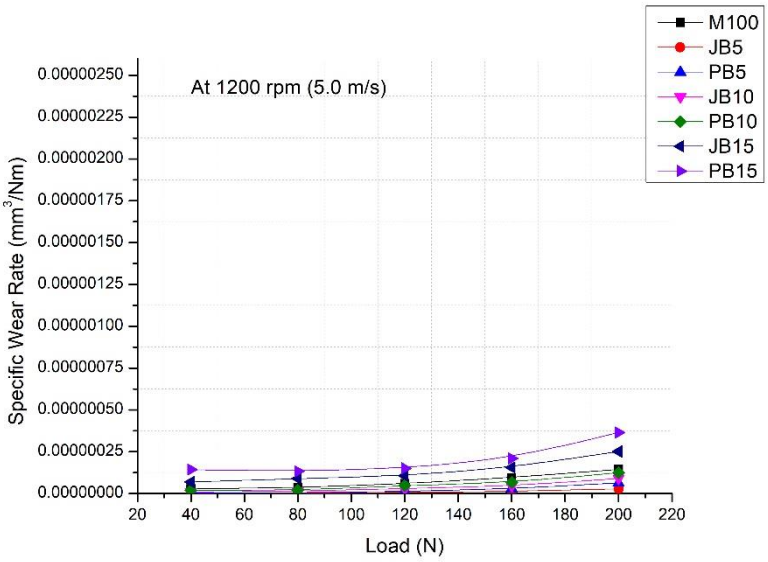
(a)


At 600 rpm (2.5 m/s)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Specific Wear Rate (mm3/Nm)
0.00000250
0.00000225
0.00000200
0.00000175
0.00000150
0.00000125
0.00000100
0.00000075
0.00000050
0.00000025
0.00000000
20
40
60
80
100
120
140
160
180
200
220
Load (N)

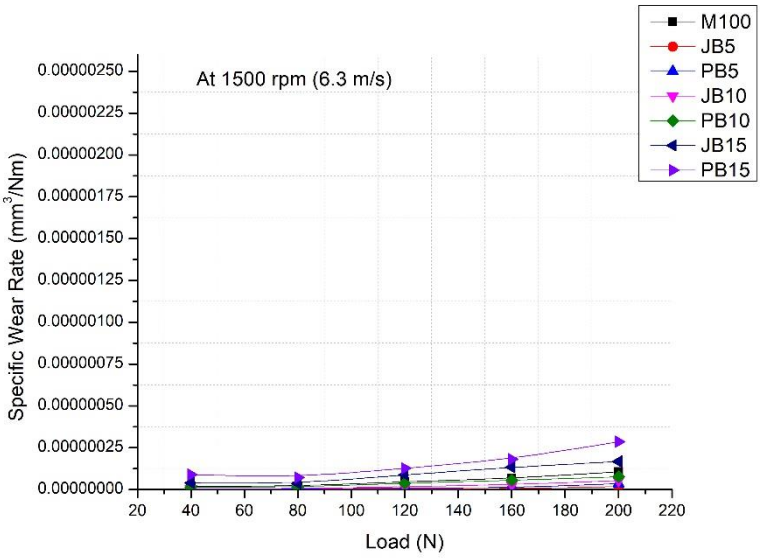
(b)


At 900 rpm (3.8 m/s)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Specific Wear Rate (mm3/Nm)
0.00000250
0.00000225
0.00000200
0.00000175
0.00000150
0.00000125
0.00000100
0.00000075
0.00000050
0.00000025
0.00000000
20
40
60
80
100
120
140
160
180
200
220
Load (N)

(c)



(d)



(e)

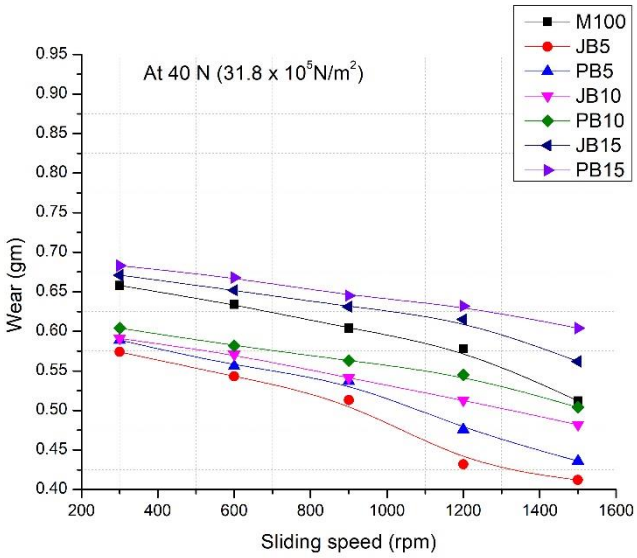
Figure 4.6. Specific wear rate for various load at different speed or velocity (a) 300 rpm (b) 600 rpm (c) 900 rpm (d) 1200 rpm (e) 1500 rpm.

On the contrary, 15 % addition exhibit higher wear rate, particularly at higher loads. About 5 to 8 % decrease in the wear of the surface was observed with the addition of pongamia and jatropha oil blends (5% and 10 %) in comparison to the conventional lubricant. The maximum SWR was observed at 200 N load and 300 rpm speed. The maximum duration of the applied forces

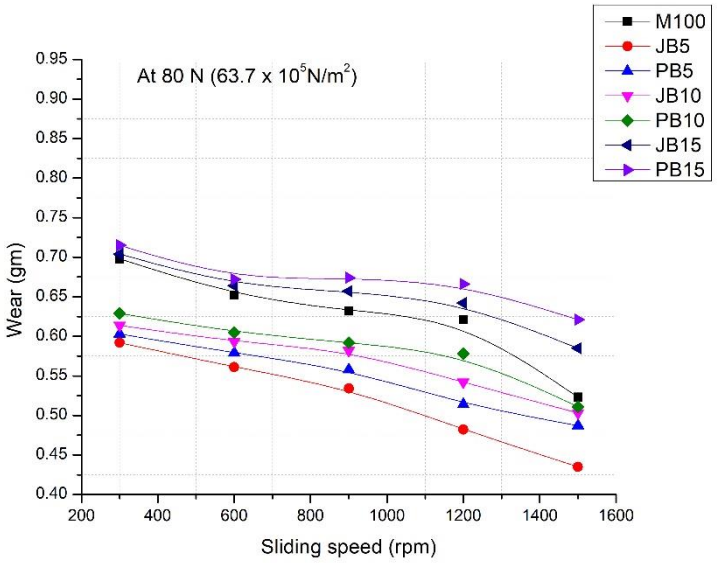
on the surface increases at a lower sliding speed which resulted in maximum wear of the material.

The presence of a higher amount of oleic acid in lubricants attributed to the wear resistivity by forming a protective film between the surfaces in sliding contact. The film was formed due to the stronger adsorption on metal surfaces and produces superior lateral collaboration between ester chains. The fatty acid consisting of a higher amount of oleic acid increases the adsorption capability of the oil due to which jatropha oil blends show better wear resistance in comparison to the pongamia oil blends [185]. Mineral oil contains additives like ZDDP to resist the wear [186]. The addition of 15 % blends results in the dilution of the properties of the additives which resulted in maximum wear among all the blends.

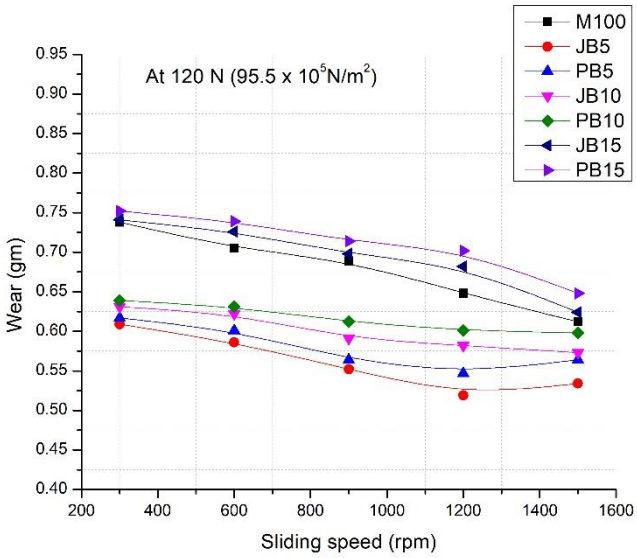
Fig. 4.7 and 4.8 depicted the weight loss of the material during sliding speed and load for various bio-lubricant blends. It can be observed clearly that the loss of material from the pin was higher for 15 % blend and least for 5 and 10 % blends as compared to the reference lubricant (M100). It can also be interpreted that the loss of material from 15 % blends was almost similar to the base lubricant. The maximum loss of material was observed at 6.3×10^{-4} N/m^2, as the increment in load, apply more pressure on the pin resulting in the increment of the loss of material [187, 188]. All the bio-lubricant blends show minimum loss of material at higher sliding speed and increase at lower sliding speed. As the speed increases time of contact between the surfaces reduces which resulted in minimum loss of material. Among blends of jatropha and pongamia, minimum loss of material was shown by jatropha oil blends which were 3.2 % lower than pongamia at different operating conditions.


At 40 N (31.8 x 10^{5}N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear (gm)
Sliding speed (rpm)
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
200
400
600
800
1000
1200
1400
1600

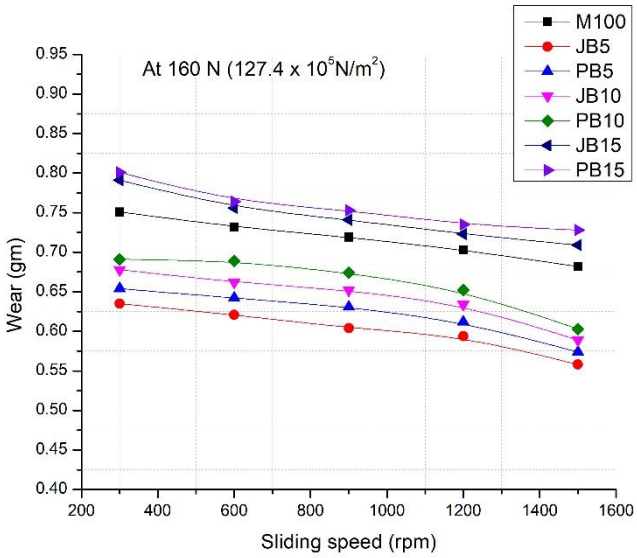
(a)


At 80 N (63.7 x 10^{5}N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear (gm)
Sliding speed (rpm)
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
200
400
600
800
1000
1200
1400
1600

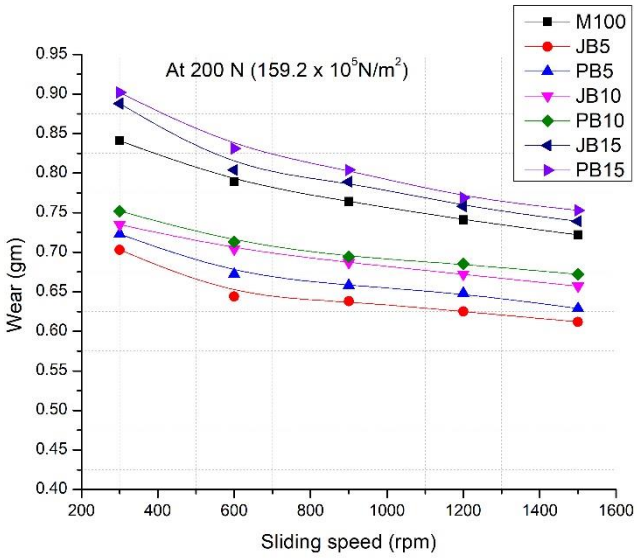
(b)


At 120 N (95.5 x 10^{5}N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear (gm)
Sliding speed (rpm)
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
200
400
600
800
1000
1200
1400
1600

(c)

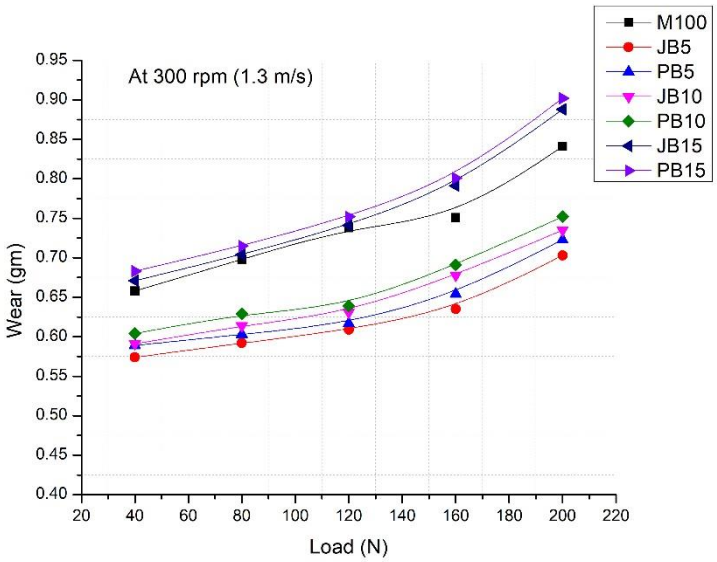

At 160 N (127.4 x 10^{5}N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear (gm)
Sliding speed (rpm)
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
200
400
600
800
1000
1200
1400
1600

(d)

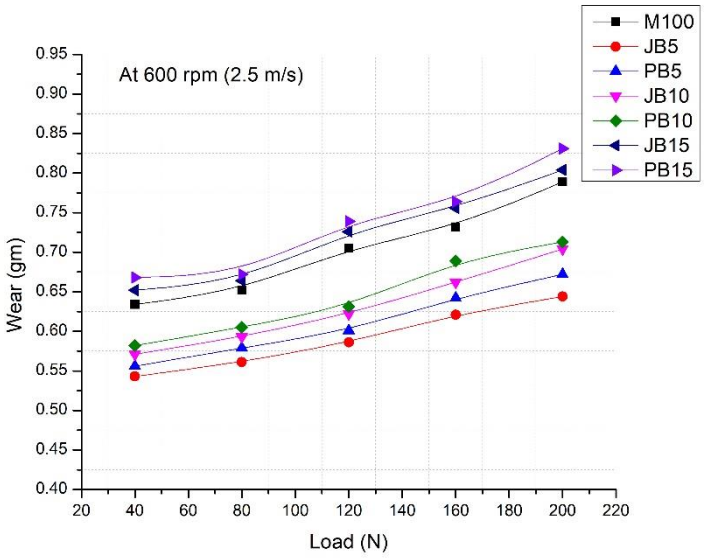


(e)

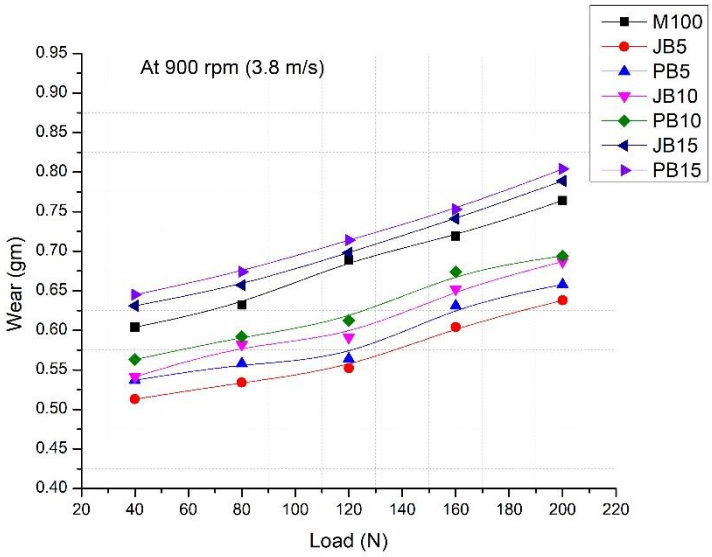
Figure 4.7. Wear of material with various sliding speed at different load (or contact pressure) (a) 40 N (b) 80 N (c) 120 N (d) 160 N (e) 200 N.



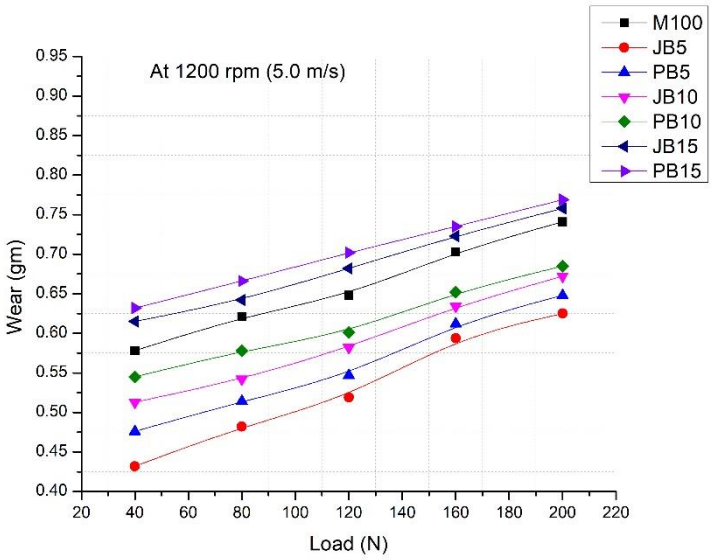
(a)


At 600 rpm (2.5 m/s)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear (gm)
Load (N)

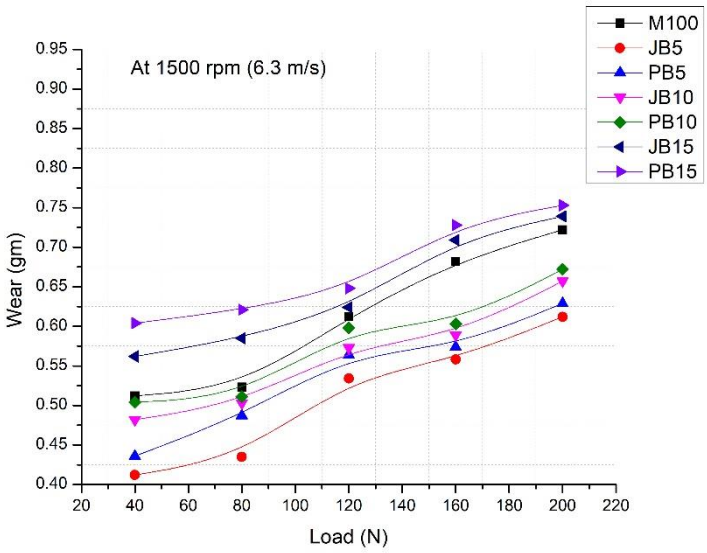
(b)


At 900 rpm (3.8 m/s)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear (gm)
Load (N)

(c)



(d)



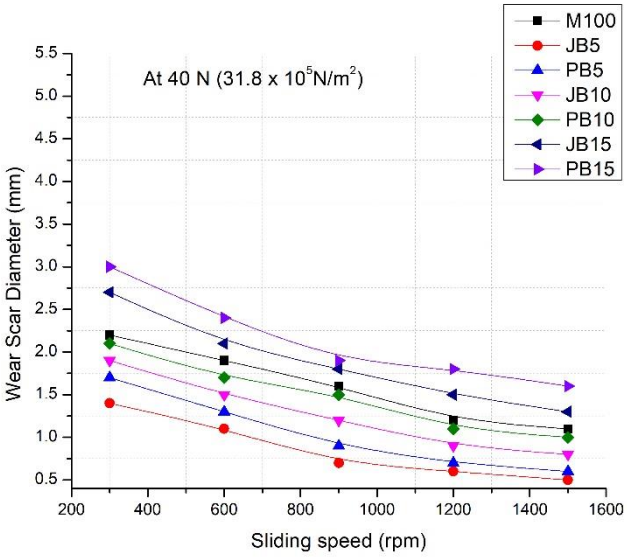
(e)

Figure 4.8. Variation of wear at different sliding speed (or velocity) with various load (a) 300 rpm (b) 600 rpm (c) 900 rpm (d) 1200 rpm (e) 1500 rpm.

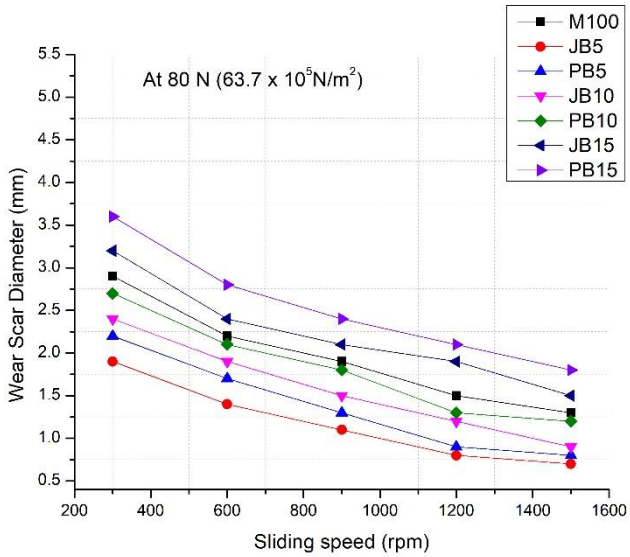
4.3. Wear scar diameter

The formation of the wear scar on the material depends on the impressions obtained on the material. It varies according to the pressure and the

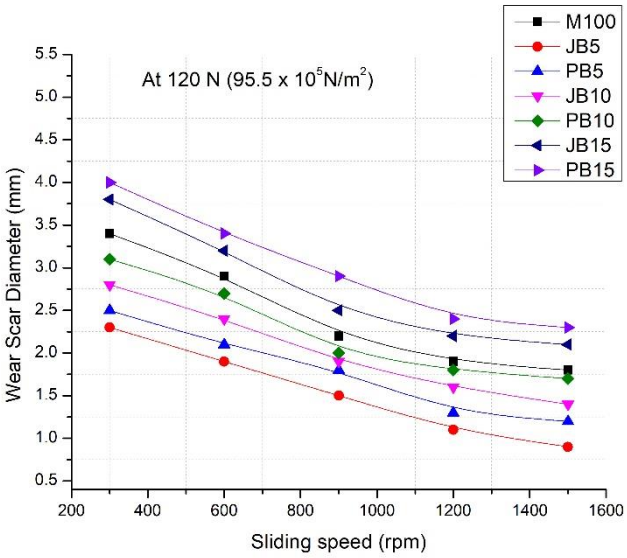
duration of the contact of the material. The erosion of the material was correlated to the inside collision of the molecules [189]. Non-edible oils have a fatty acid composition which provides completely packed structure resulting in the minimum release of the molecules. The detailed description of the wear scar diameter as shown in Fig. 4.9 and 4.10.



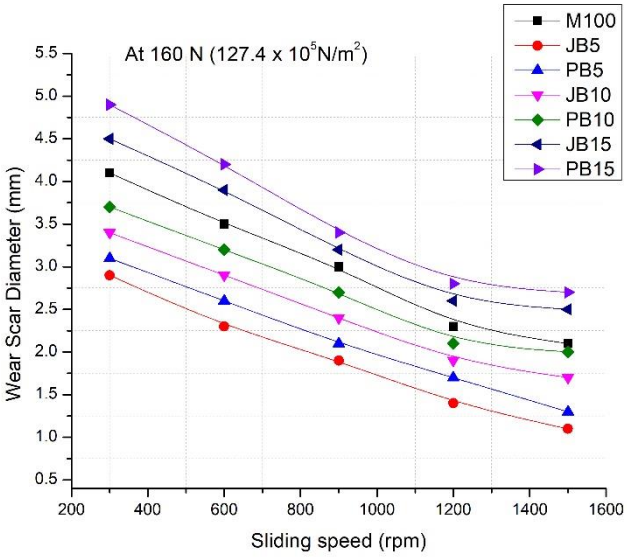
(a)



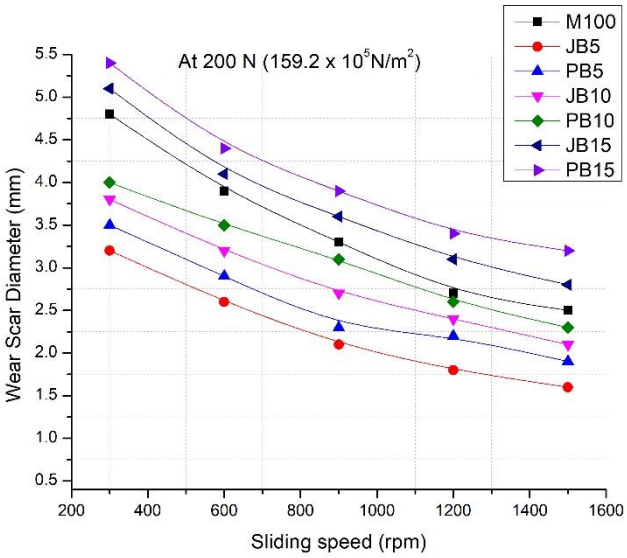
(b)


At 120 N (95.5 x 10^5N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear Scar Diameter (mm)
Sliding speed (rpm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
200
400
600
800
1000
1200
1400
1600

(c)


At 160 N (127.4 x 10^5N/m^2)
M100
JB5
PB5
JB10
PB10
JB15
PB15
Wear Scar Diameter (mm)
Sliding speed (rpm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
200
400
600
800
1000
1200
1400
1600

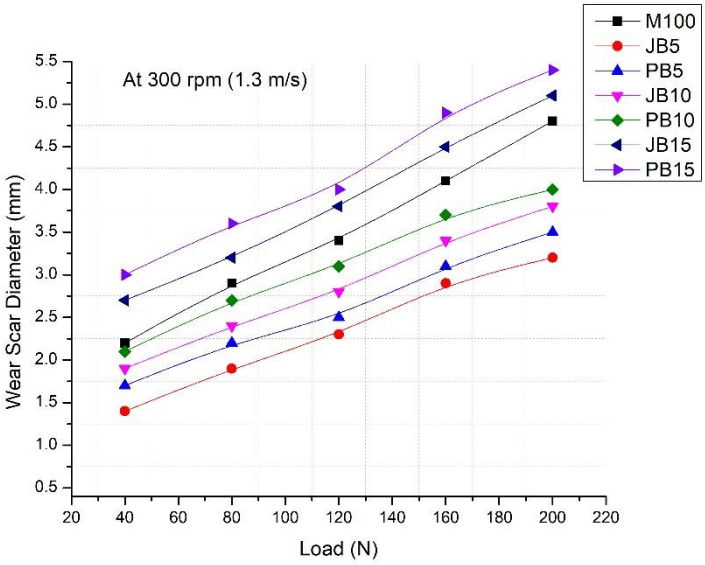
(d)



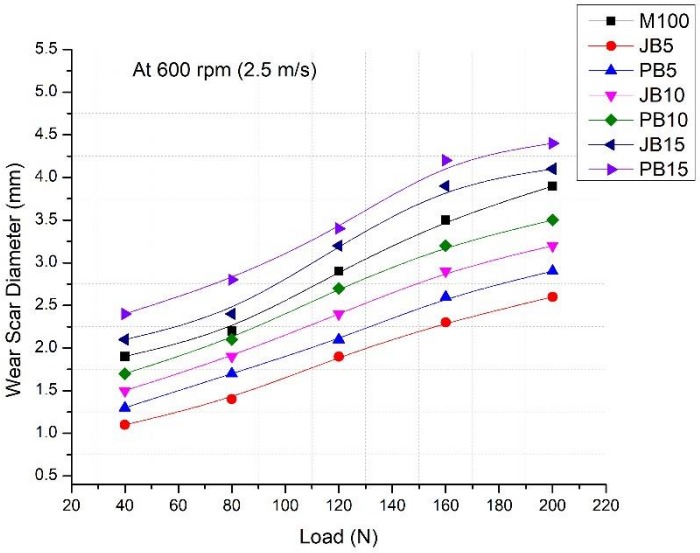
(e)

Figure 4.9. Wear scar diameter at different load (or contact pressure) (a) 40 N (b) 80 N (c) 120 N (d) 160 N (e) 200 N.

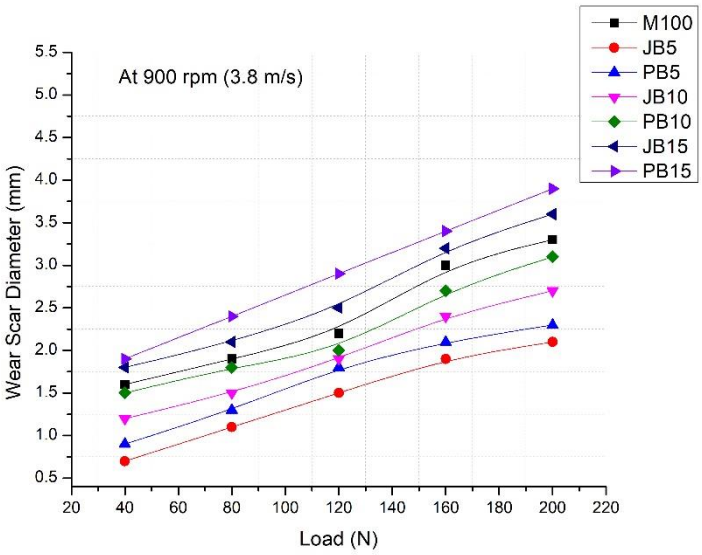
It is well-known fact that when the normal load increases, the pressure on the surface resulting in the formation of wear scar on the surface. A maximum wear scar diameter was observed at higher load. The ranges in the wear scar diameter (WSD) were 1.5 to 3 mm, 1.8 to 3.6 mm, 2.3 to 4.1 mm, 2.9 to 5 mm and 3.4 to 5.6 mm at 40 N, 80 N, 120 N, 160 N, 200 N load respectively. The 5 % and 10 % blends show minimum WSD among all the blends.



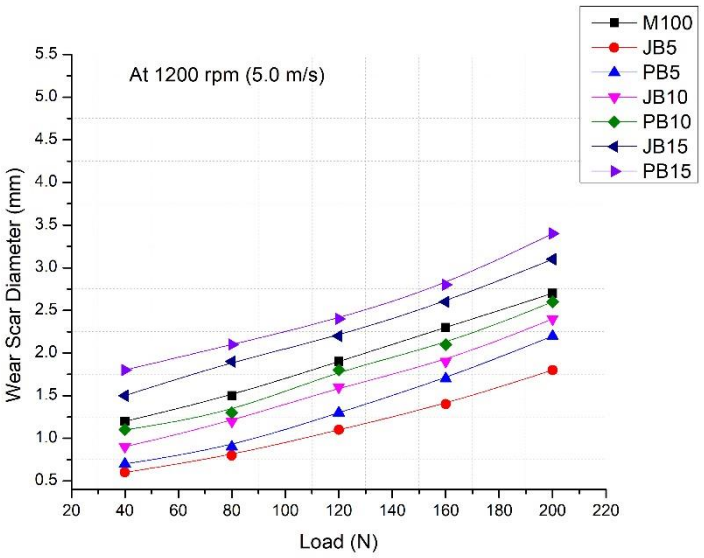
(a)


At 600 rpm (2.5 m/s)
Wear Scar Diameter (mm)
Load (N)
M100
JB5
PB5
JB10
PB10
JB15
PB15

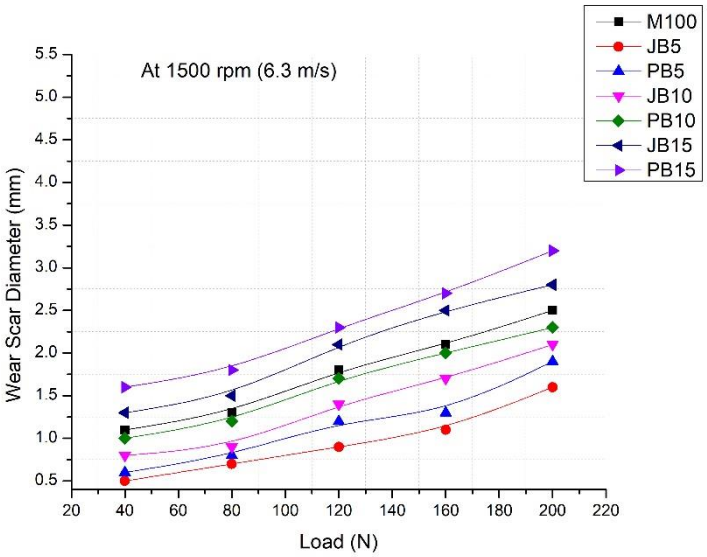
(b)


At 900 rpm (3.8 m/s)
Wear Scar Diameter (mm)
Load (N)
M100
JB5
PB5
JB10
PB10
JB15
PB15

(c)



(d)



(e)

Figure 4.10. Wear scar diameter at different speed (or velocity) (a) 300 rpm (b) 600 rpm (c) 900 rpm (d) 1200 rpm (e) 1500 rpm.

Wear scar diameter decreases with an increase in sliding speed. Maximum WSD obtained at 300 rpm and minimum at 1500 rpm. The range of the scar varies from 2.6 to 5.3 mm at a higher load during 300 rpm and 1.2 to 3 mm during 1500 rpm speed. The 5 % blend of jatropha and pongamia shows a

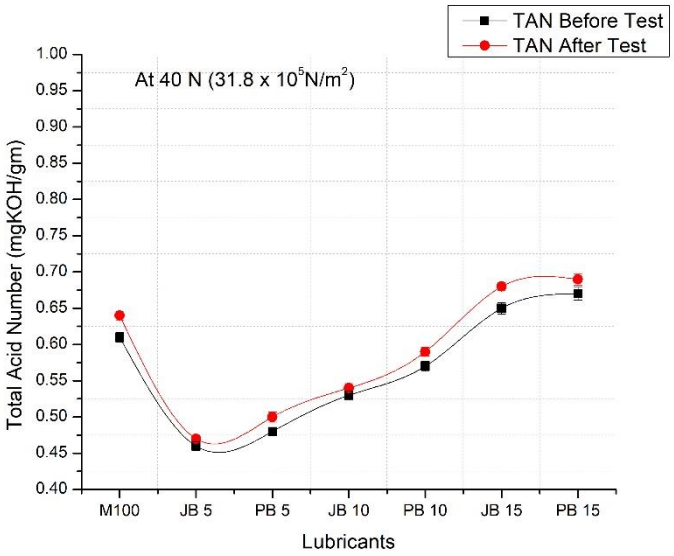
difference of about 0.5 mm at 2.51 m/s and 0.2 mm at 12.56 m/s. An excellent lubricant film was formed due to the formation of trimethylolpropane (TMP) triester up to 5% and 10% blends. The film thickness increases due to the long-chain fatty acid TMP ester's in comparison to the mineral oil. The protective film results in the formation of a smooth surface contributing towards a minimum wear scar diameter. With an increase in the blending ratio after a certain limit, the formation of triester reduces resulting in a thin film formation which ultimately increases wear scar diameter.

4.4. Lubricant degradation analysis

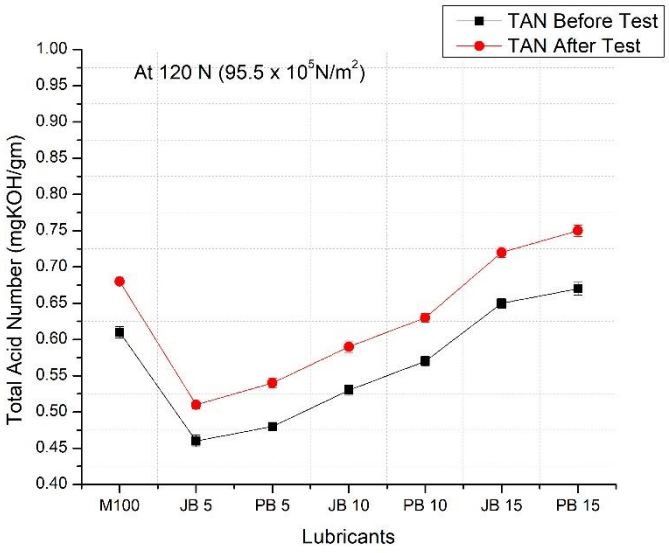
The presence of acidity in the lubricants promoted their degradation depending on the experimental conditions. More amount of acidic content reduces the viscosity of the lubricants and promotes wear of the surface. Fig. 4.11 discussed the variation of total acid number with different blends at various contact pressure (load). The variation of total acid number was obtained at 40 N, 120 N, and 200 N load. The maximum speed of 1500 rpm was considered for all the conditions applied. The higher variation in the acidic number was obtained at a higher load. The minimum drop in the acidic value was obtained at 5 % and 10 % blends in comparison to the mineral oil (M100). A significant difference was obtained at PB 15 and JB 15 blends as compared to other blends. An acidic component increases due to the depletion of additives when the load is applied during lubricant usage indicating maximum proneness of the surfaces to the corrosion. Viscosity was also one of the major factors responsible for the degradation of the lubricant. The 15 % blends result in the production of more acidic value as compared to the other blends because the properties of this blends gets depleted due to more blending and the formation tendency of acidic content increases [40].

The elemental analysis of the oil was performed by using flame atomic absorption spectrometry to determine the presence of metals in the lubricating oil before and after conducting the test. The degraded oil was taken for the analysis after conducting a test at 40 N, 120 N and 200 N load while keeping sliding speed constant at 1500 rpm. The condition was preferred based on the operating parameters and the studies quoted in the literature [135, 190]. Fig 4.12

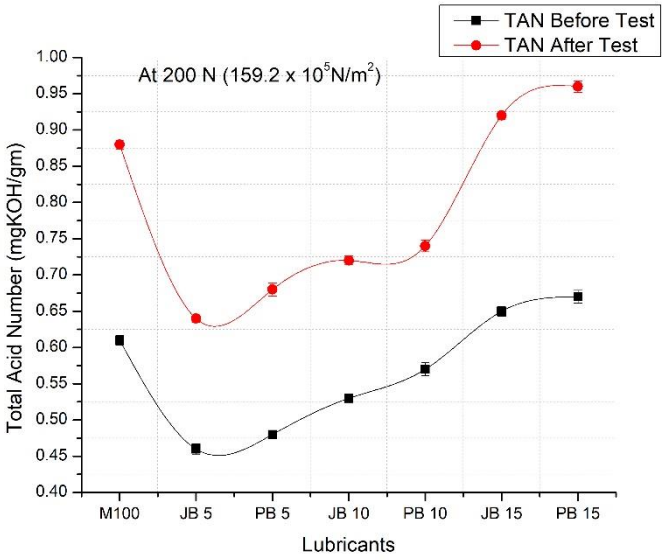
shows the details of the elements present in the degraded oils. It can be noticed that the mineral oil contains higher traces of aluminium, silicon and other elements with comparison to the jatropha and pongamia oil blends up to 10%. The higher amount 0f elements with comparison to other blends were detected at higher blends for both the oils. With an increase in load, the amount of elements present in the oil increased due to more contact pressure acting on the metals parts. Due to lower hardness of the aluminium pin, the extraction of aluminium from the pins was much higher than steel plate. The changes in other elements were observed less with comparison to the main constituents. It is clear from the elemental analysis that, most of the elements were decreased after the test by oxidizing and the chemical interaction among the elements present in the lubricant.



(a)

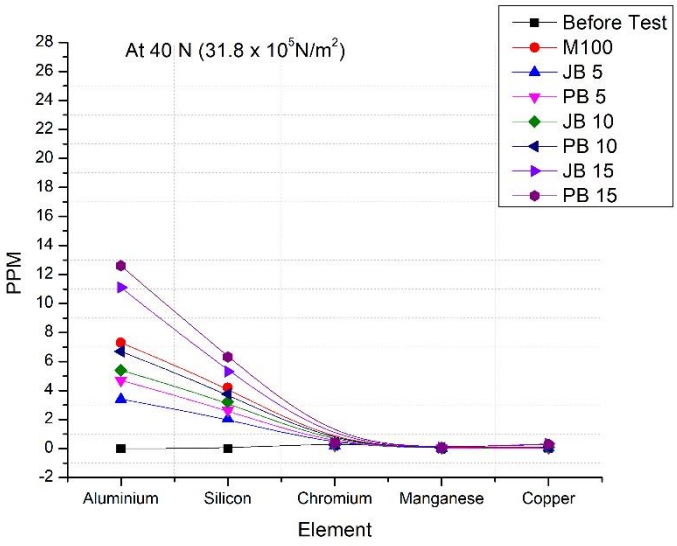


(b)

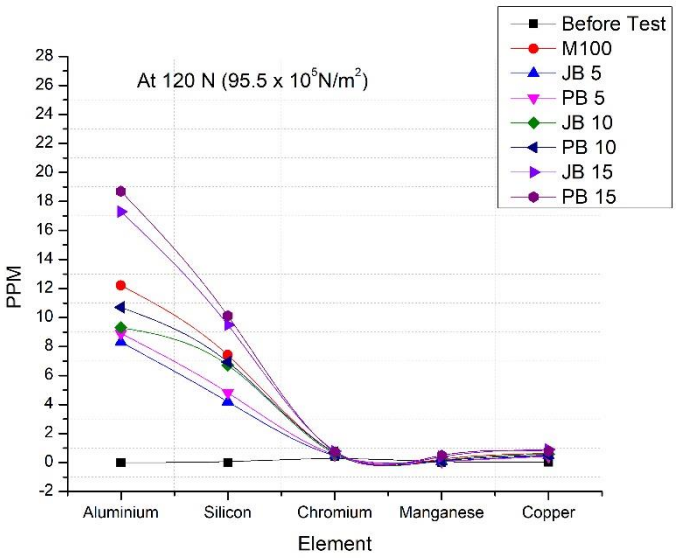


(c)

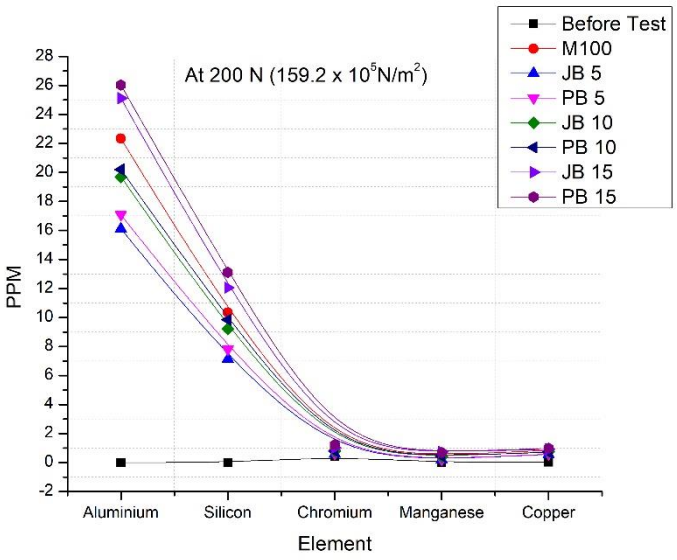
Figure 4.11. Total acid number of different bio-lubricants at load (or contact pressure) (a) 40 N (b) 120 N (c) 200 N.


At 40 N (31.8 x 10^5N/m^2)
Before Test
M100
JB 5
PB 5
JB 10
PB 10
JB 15
PB 15
PPM
Element
Aluminium
Silicon
Chromium
Manganese
Copper

(a)


At 120 N (95.5 x 10^5N/m^2)
Before Test
M100
JB 5
PB 5
JB 10
PB 10
JB 15
PB 15
PPM
Element
Aluminium
Silicon
Chromium
Manganese
Copper

(b)



(c)

Figure 4.12. Elemental oil analysis at loads (or contact pressure) (a) 40 N (b) 120 N (c) 200 N.

4.5. Correlation with the engine parameters

4.5.1. Response surface methodology

Response surface methodology is one of the optimization technique which can be utilized for the development of the models by implementing several factors [176]. In this study, response parameters was optimized based on the input parameters and model was generated which correlated the relation between the response parameters related to the tribometer and diesel engine. Table 4.1 show the design of experiment obtained using Minitab software. The level of the input parameters considered during this study has already been discussed in the materials and method section. Equation 4.1 shows the relation between response parameters and the input parameters.

$$R = \beta_o + \sum_{i=1}^{4} \beta_i I_i + \sum_{i=1}^{4} \beta_{ii} I_i^2 + \sum_{i-1}^{k-1} \sum_{j\geq 1}^{k} \beta_{ij} I_i I_j \qquad (4.1)$$

Where, R is the response (estimated), I_i, I_j are variables (independent), β_o is the intercept coefficient, β_i are the i_{th} linearity coefficient, β_{ii} is coefficient of quadratic and β_{ij} is coefficient of interaction (linear by linear). The analysis of variance (ANOVA) analysis was applied to test the model validity and to determine the significance of each parameters considered. The

value of F-test was obtained while considering the individual effect of parameters and their interaction. The degree of fitness of the model depends on F-values with p value < 0.05. The check the model precision with validity, value of R^2 adjusted, R^2 and R^2 predicted, and lack fit were inspected. To observe the input-output interaction and to evaluate the optimal solutions, the form-fitting quadratic polynomial equation was expressed as a response surface.

Table 4.1.

Design of experiment using RSM.

Run order	**Speed (rpm)**	**Load** (N)	**Lubricant (%)**	**Wear (tribometer) (gm)**	**Wear (engine) (gm)**
1	0	-1	-1	1.588	0.612
2	0	0	0	1.632	0.721
3	0	0	0	1.612	0.678
4	-1	0	1	1.741	0.745
5	1	1	0	1.594	0.662
6	0	1	-1	1.648	0.714
7	1	-1	0	1.608	0.679
8	0	0	0	1.612	0.662
9	1	0	-1	1.594	0.658
10	-1	0	-1	1.778	0.863
11	-1	1	0	1.657	0.749
12	0	1	1	1.612	0.714

13	1	0	1	1.634	0.635
14	-1	-1	0	1.678	0.741
15	0	-1	1	1.512	0.602

4.5.2. Statistical modelling

Based on the design of experiments obtained from the Box-Behnken design of response surface methodology, experiment was performed for the output parameters as shown in Table 4.1. The experimental output data related to Wear (Tribometer) and Wear (Engine) was used to develop the statistical models, which relates the pertinent input parameter to the required output responses. Generally used models such as; linear, and quadratic were tested and scrutinized by analysis of variance (ANOVA) to obtain the good statistical connections between input and output variables. The ANOVA analysis suggests that the modified quadratic model correlates the investigational data very well for both the output parameters as compared to the other tested models. Hence, only the quadratic models for both output parameters are discussed here, properly. Figs. 4.13 and 4.14 shows the residual plots obtained for the output responses. It can be seen from the plots that there is random distribution of the residuals in both figures and they are not following any definite pattern. Therefore, it can be concluded that the there is no model insufficiency based on the residual pattern and the model is adequate enough to predict the responses at a confidence level of 95%.The suggested models for output responses, wear (tribometer) and wear (engine) are represented by Eqns. 4.2, 4.3, and 4.4, respectively.

Wear (tribometer) = 2.389+0.000160*speed+0.002260*load-0.02518*lubricant-0.000000*speed^2-0.000004*load^2+0.003175*lubricant^2-0.000000*speed*load- 0.000005* speed*lubricant - 0.000040*load*lubricant (4.2)

Wear (engine) = 3.599+0.000126*speed+0.00096*load-0.02488*lubricant-0.000000*speed^2-0.000001*load^2+0.002755*lubricant^2-0.000000*speed*load-0.000008*speed*lubricant+0.000006*load*lubricant

(4.3)

Wear (engine) = 1.411 + 0.8688*Wear (tribometer) (4.4)

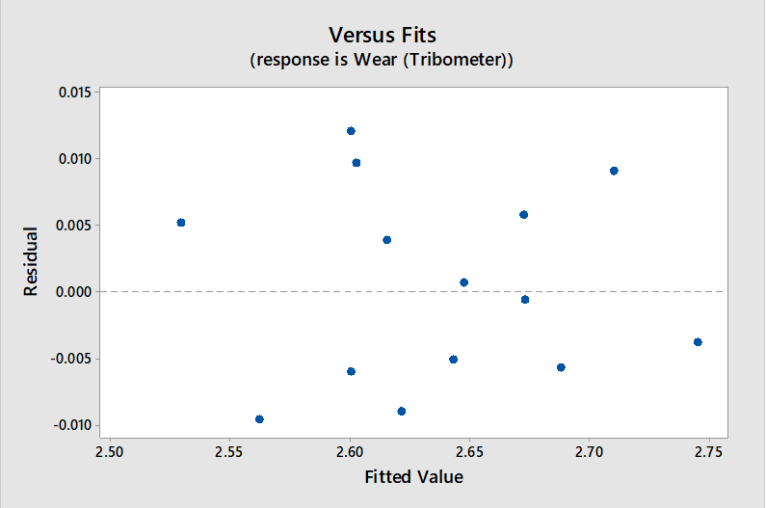


Figure 4.13. Plot of residual value vs fitted values for wear (tribometer).

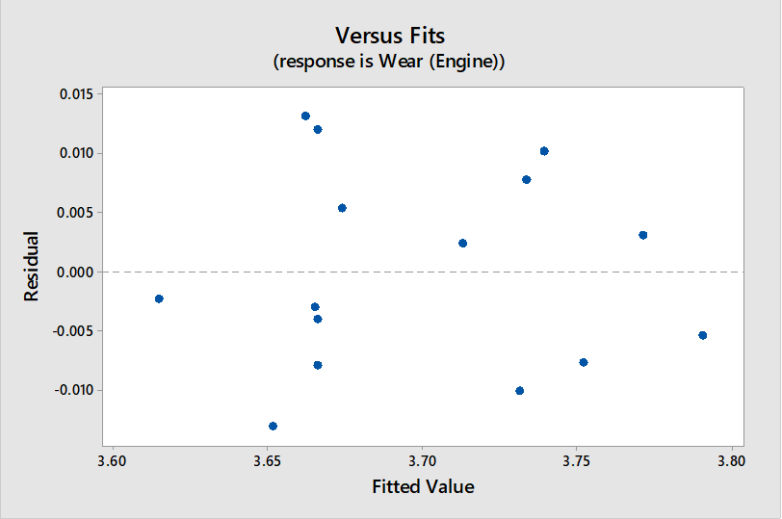


Figure 4.14. Plot of residual value vs fitted values for wear (engine).

ANOVA analysis based on F-test was applied to the developed model to assess the importance of each model terms. Higher F-value indicates that alteration in output can be explained by the developed model and the associated *p*-value was also used to determine, whether 'F' is adequate to direct statistical

significance. The *p*-values below than 0.05 indicate that the developed model and the terms are significant (statistically). The F-valve and p-value of the quadratic model developed for wear recommended that some individual, second order and all interaction terms such as are insignificant, whereas all other terms are significant. The value of statistical correlation coefficients for wear (tribometer) and wear (engine) is shown in Table 4.2. The 'R^2' value provides the fraction of total alteration in the output expected by developed model and 0.9813 for quadratic model confirms a good fit to data (experimental). The value of 'R^2 adjusted' for the suggested model is 0.9837 that is also high and supports a good correlation between predicted and experimental value. The 'R^2 predicted' value for the present model is 0.9712 and suggests excellence of the present model to predict the value of specific wear rate. Similarly, the F-valve and *p*-value of the quadratic model developed aimed at wear recommended that interaction of the parameters between them are insignificant, whereas all other terms are significant. The values of statistical correlation coefficients, 'R^2', 'adjusted R^2' and 'predicted R^2', for a quadratic model (Eq. (4.3, 4.4 and 4.5) give the idea about the accuracy of the suggested model as shown in Table 4.2. Moreover, the ANOVA table for wear (tribometer) and wear (engine) are given in Table 4.3 and 4.4. Consequently, attaining all the above particulars that practiced goodness of fit of the model into concern, it can be decided that the quadratic model is the best model out of linear, and quadratic model.

Table 4.2.

Statistical correlation coefficients for output variables.

	Wear (tribometer)	**Wear (engine)**
R-square	0.9813	0.9844
Adjusted *R*-square	0.9837	0.9864
Predicted *R*-square	0.9712	0.9732

Table 4.3.

ANOVA table for wear (tribometer).

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	***p*-Value**
Model	9	0.045458	0.005051	35.43	0.001

Linear	3	0.020174	0.006725	47.17	0.000
Speed	1	0.002701	0.002701	18.95	0.007
Load	1	0.012013	0.012013	84.27	0.000
Lubricant	1	0.005460	0.005460	38.30	0.002
Square	3	0.024658	0.008219	57.66	0.000
Speed*Speed	1	0.000162	0.000162	1.14	0.335
Load*Load	1	0.000325	0.000325	2.28	0.192
Lubricant*Lubricant	1	0.023263	0.023263	163.19	0.000
2-Way Interaction	3	0.000626	0.000209	1.46	0.330
Speed*Load	1	0.000016	0.000016	0.11	0.751
Speed*Lubricant	1	0.000210	0.000210	1.47	0.279
Load*Lubricant	1	0.000400	0.000400	2.81	0.155
Error	5	0.000713	0.000143		
Lack-of-Fit	3	0.000497	0.000166	1.53	0.418
Pure Error	2	0.000216	0.000108		
Total	14	0.046170			

Table 4.4.

ANOVA table for wear (engine).

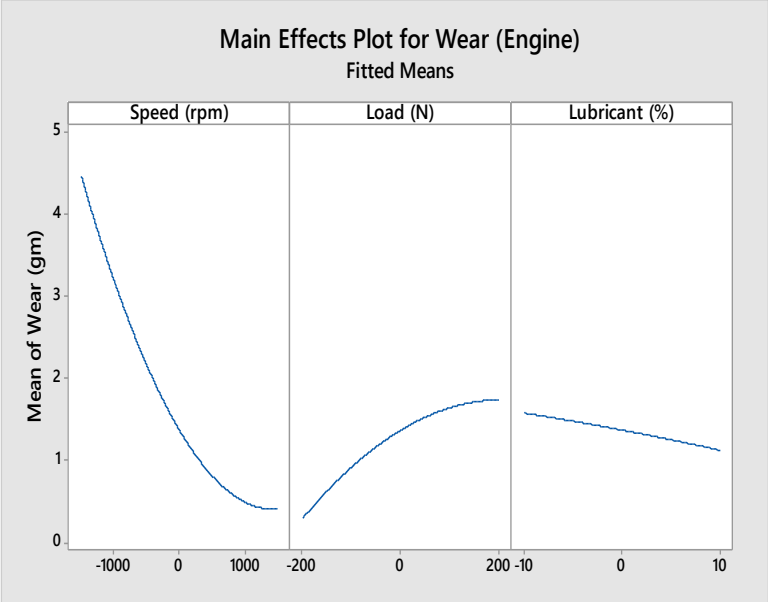
Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	***p*-Value**
Model	9	0.036191	0.004021	20.50	0.002
Linear	3	0.017519	0.005840	29.77	0.001
Speed	1	0.003828	0.003828	19.52	0.007
Load	1	0.005941	0.005941	30.29	0.003
Lubricant	1	0.007750	0.007750	39.51	0.001
Square	3	0.018014	0.006005	30.61	0.001

Speed*Speed	1	0.000079	0.000079	0.40	0.554
Load*Load	1	0.000007	0.000007	0.04	0.858
Lubricant*Lubricant	1	0.017515	0.017515	89.30	0.000
2-Way Interaction	3	0.000658	0.000219	1.12	0.424
Speed*Load	1	0.000049	0.000049	0.25	0.638
Speed*Lubricant	1	0.000600	0.000600	3.06	0.141
Load*Lubricant	1	0.000009	0.000009	0.05	0.839
Error	5	0.000981	0.000196		
Lack-of-Fit	3	0.000757	0.000252	2.25	0.322
Pure Error	2	0.000224	0.000112		
Total	14	0.037172			

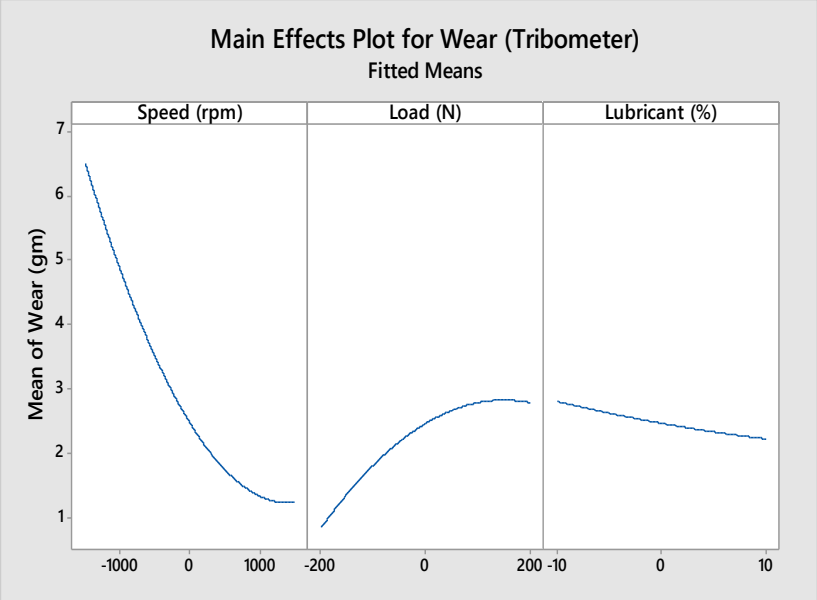
4.5.3. Effect of Individual parameters

The main effect plots for wear (tribometer) and wear (engine) are shown in Figs. 4.15 (a) and (b) respectively. With help of these plots, it is easy to determine the best combination of the input variables for obtaining an optimal results. Figs. 4.15 (a) and (b) shows the mean values obtained for the response wear in which lowest are the feasible results at which minimum wear of the surfaces can be obserevd.

It could be seen in Figs. 4.15 (a) and (b) that the optimum process condition for both the wear (tribometer) and wear (engine) became $A_3B_1C_3$ for main control factors. The optimum conditions for the wear (tribometer) and wear (engine) are sliding speed with level 3, load with level 1 and lubricant with level 3.



(a)



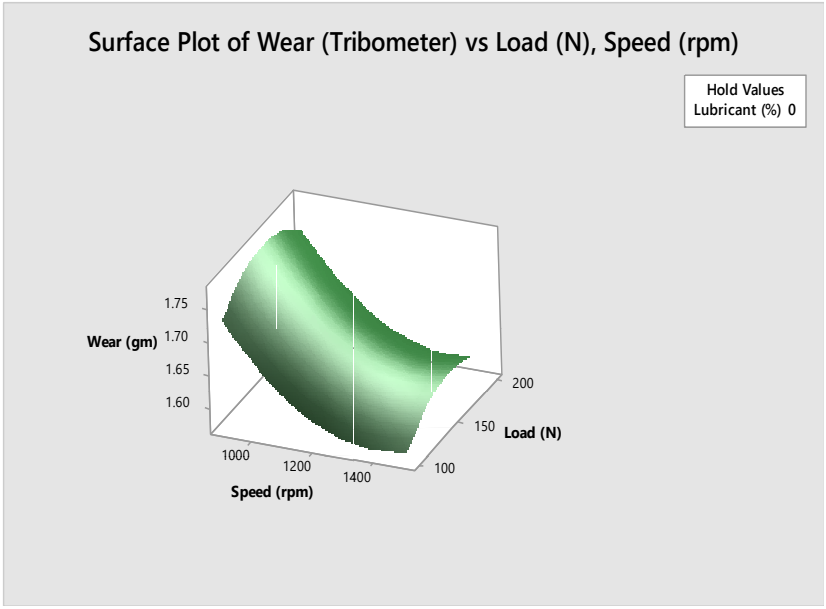
(b)

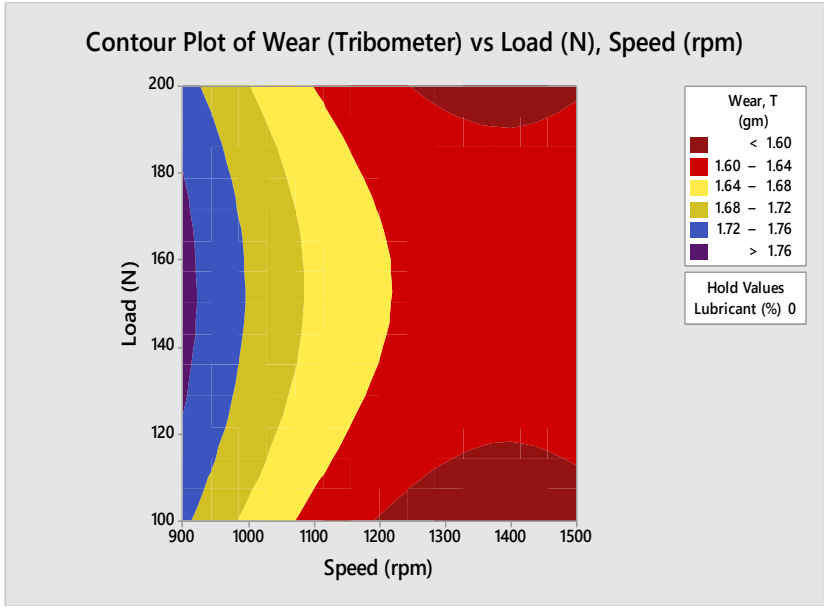
Figure 4.15. Main effect plot for (a) wear (tribometer) (b) wear (engine).

The 3D surface plot and contour plots of lubricant, load, and speed and their combined effect on wear (tribometer) and wear (engine) are shown in Figs. 4.16 (a-c) and 4.17 (a-c). It can be found that wear increases with the increase in load. At lower load conditions, there is a marginal change in wear rate for all the tested feedstock's. But, at higher load conditions, 5 % and 10% blend exhibit lower wear as compared to the mineral oil. It can be perceived from the trends

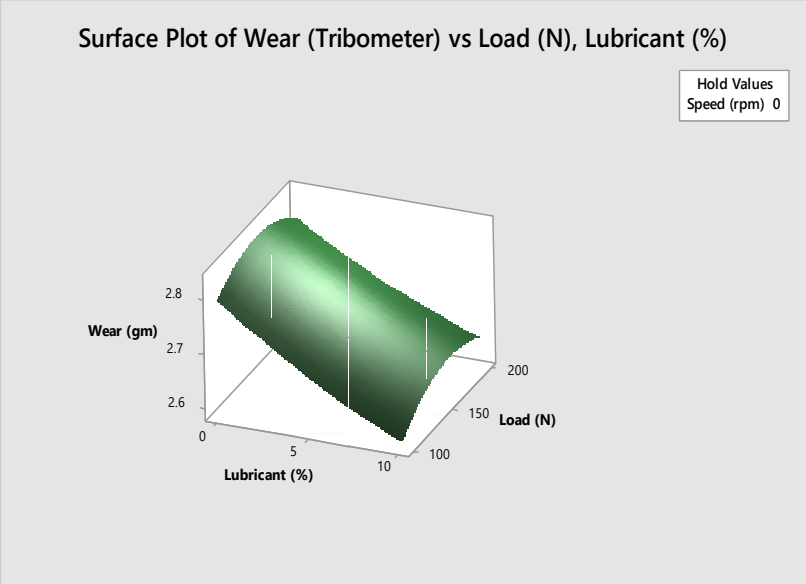
that wear is influenced by operating parameters i.e., load, the concentration of bio-lubricant and sliding speed. Maximum wear was shown at lower speed and minimum at a higher speed. From the contour plots of Figs 4.16 and 4.17, it was observed that the region of maximum wear deceits towards the maximum load, minimum speed and mineral oil. Owing to its amphiphilic properties, bio-lubricant adsorbs to surface of the metal which is endowed by the ester affectivities along with hydrocarbon chains (long) of residue acid [44, 51, 112]. As amphiphiles are adsorbed on the surface, there is adhesive interaction between ester molecules and mating surface due to its dispersive and dipole-dipole interaction between adsorbed molecules and long-chain length as well as a degree of unsaturation of bio-lubricant [191]. In addition, oxygen molecules presence and double bonds in bio-lubricant are found to be beneficial for improving lubricity. The existence of minor components such as tocopherol and phospholipids also increases the lubricity of biodiesel as these components act as antioxidants. The phosphorous soap at the surfaces provided by surface-active compounds i.e. Phospholipids also enhances the lubricity. The 5 % and 10 % blend shows improved results at higher sliding velocity. Methyl esters are more hygroscopic than mineral oil. Due to this, it ingests more moisture and inclined to oxidation. The oxidation process generates water and fatty acids like propionic acid, acetic acid, caproic acid etc [36]. The reasons for oxidation might be ascribed to the exposure of bio-lubricant to air at the elevated temperature condition. The different chemical species i.e. carboxylic acids, ketones, aldehydes etc are formed at higher sliding velocity when esters react with oxygen in the presence of air. As the contents of the bio-lubricant increase in the blends, the formations of these carbonyl groups enhance and hence, results in the increase in oxidation. These products produced during oxidation have highly affected viscosity and hence improve lubricity. Conversely, it was also reported that, the formation of acids during oxidation enhances corrosive wear and hence, adversely affected the lubricity. But, the impact of this corrosive wear is less effective [192]. Though, the enhancement in viscosity through oxidation improves lubricity in short term bench tests. However, the oxidation leads to degradation of lubricant which diminishes the performance of it in long term tests. So, the effect of oxidation on tribological performance

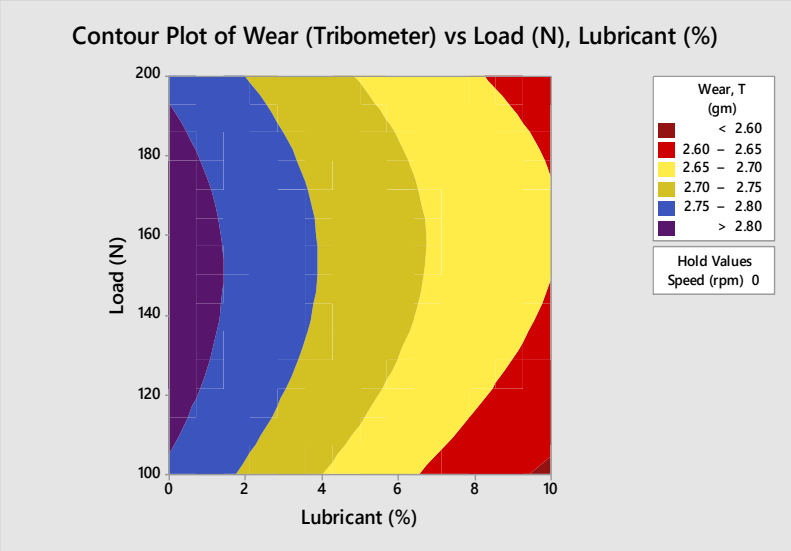
of engine is crucial. A strong relation of tribology performance possesses with viscosity of oil and its variation. Boundary layer formation takes place on the surface becomes thinner and less effective due to lower viscosity. This enhanced the interaction of surfaces that rise thermal energy which leads to increase in friction and wear. Moreover, higher contents of bio-lubricant degrade products react with the additives i.e. Zinc Dialkyl Dithio Phosphate (ZDDP) especially at higher load. Mostly, wear enhance with the increase in load. It has been noted that with increase in applied load, wear increases due to failure of lubricating film and incipient scuffing occurs.



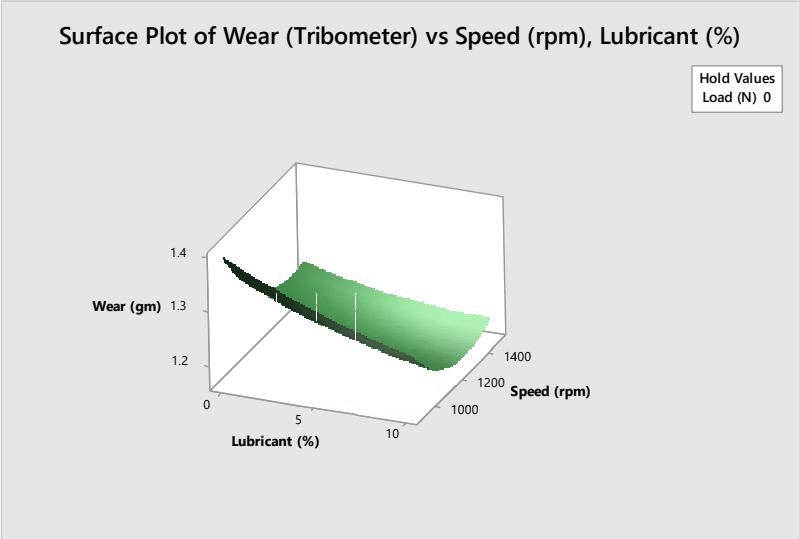


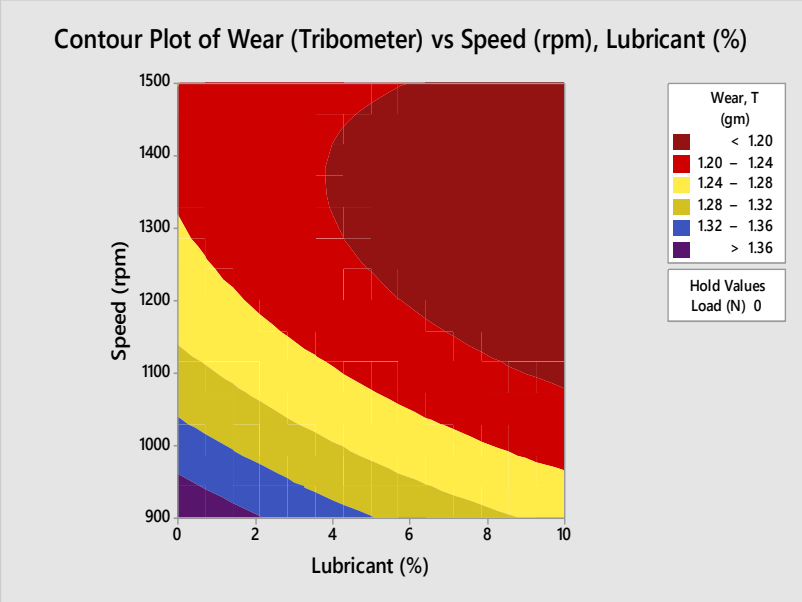
(a)


Surface Plot of Wear (Tribometer) vs Load (N), Lubricant (%)
Hold Values
Speed (rpm) 0
Wear (gm)
2.8
2.7
2.6
0
5
10
Lubricant (%)
100
150
200
Load (N)


Contour Plot of Wear (Tribometer) vs Load (N), Lubricant (%)
Load (N)
200
180
160
140
120
100
0
2
4
6
8
10
Lubricant (%)
Wear, T (gm)
< 2.60
2.60 – 2.65
2.65 – 2.70
2.70 – 2.75
2.75 – 2.80
> 2.80
Hold Values
Speed (rpm) 0

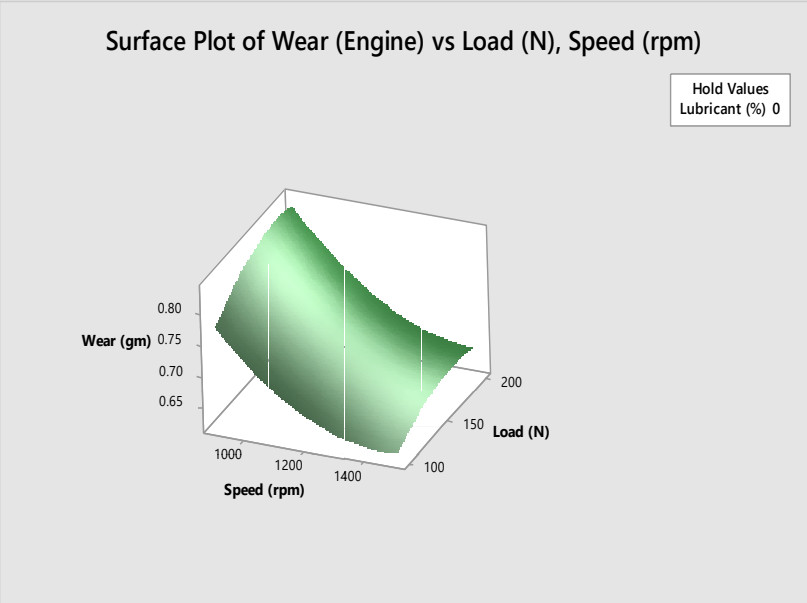
(b)

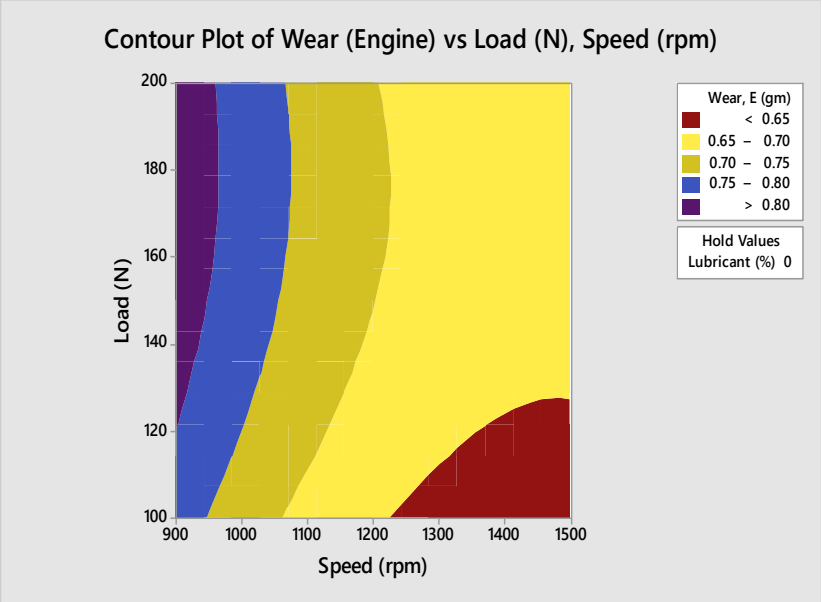

Surface Plot of Wear (Tribometer) vs Speed (rpm), Lubricant (%)
Hold Values
Load (N) 0
Wear (gm)
1.4
1.3
1.2
0
5
10
Lubricant (%)
1000
1200
1400
Speed (rpm)



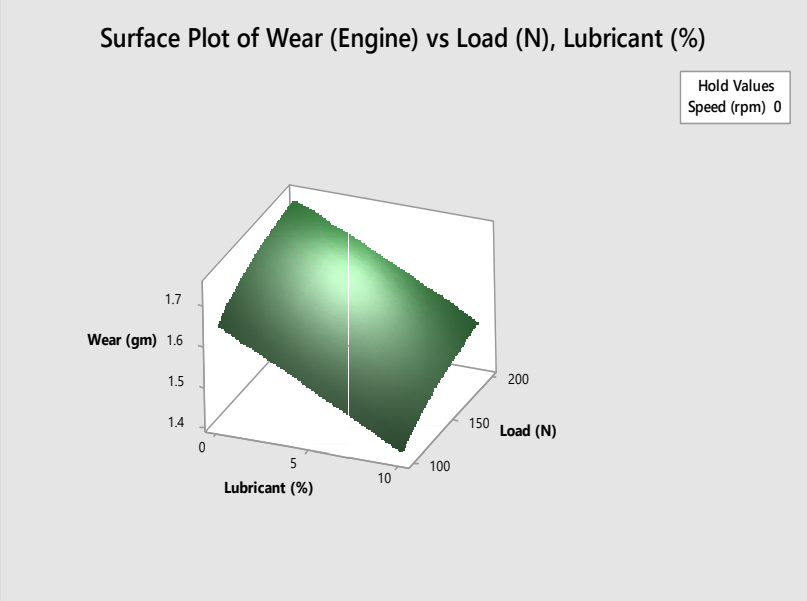
(c)

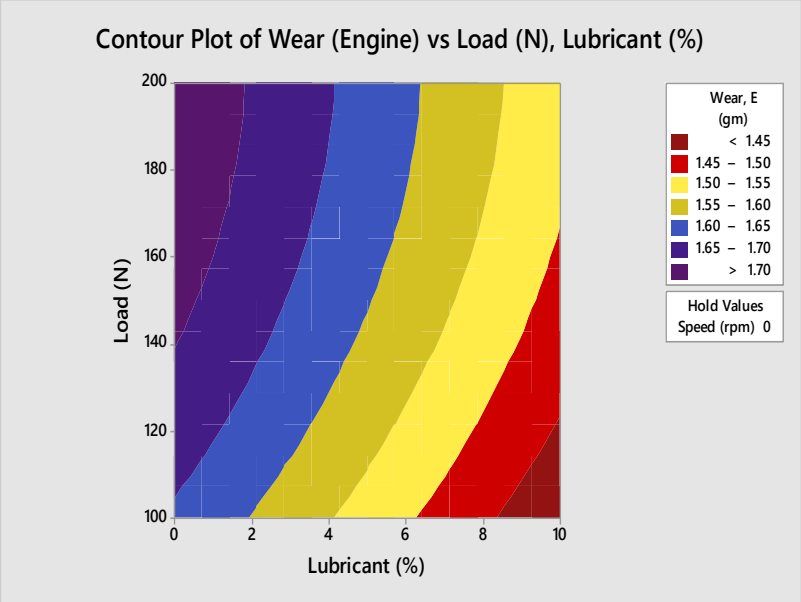
Figure 4.16. Surface plot and contour plot for the effect of individual parameters on wear (tribometer) (a) load vs speed (b) load vs lubricant (c) load vs lubricant.



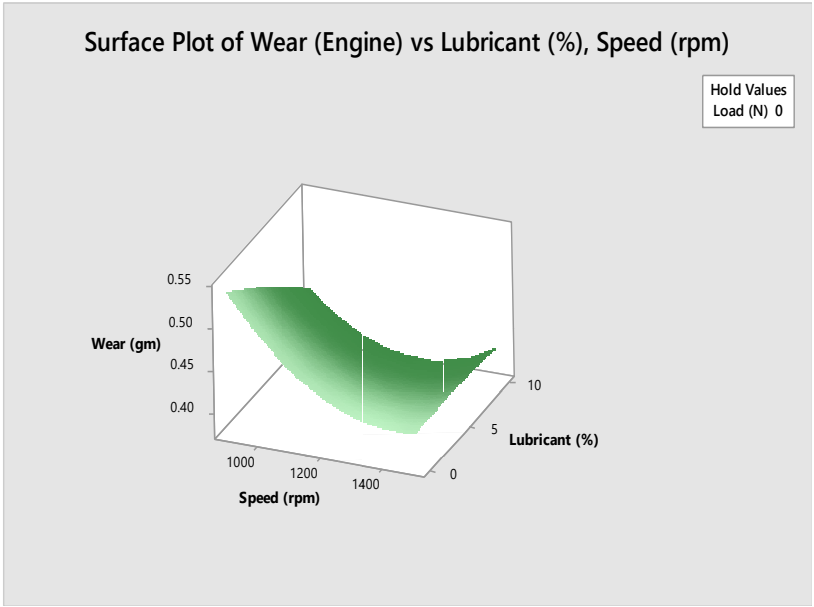

Contour Plot of Wear (Engine) vs Load (N), Speed (rpm)
Wear, E (gm)
< 0.65
0.65 – 0.70
0.70 – 0.75
0.75 – 0.80
> 0.80
Hold Values
Lubricant (%) 0
Load (N)
200
180
160
140
120
100
900
1000
1100
1200
1300
1400
1500
Speed (rpm)

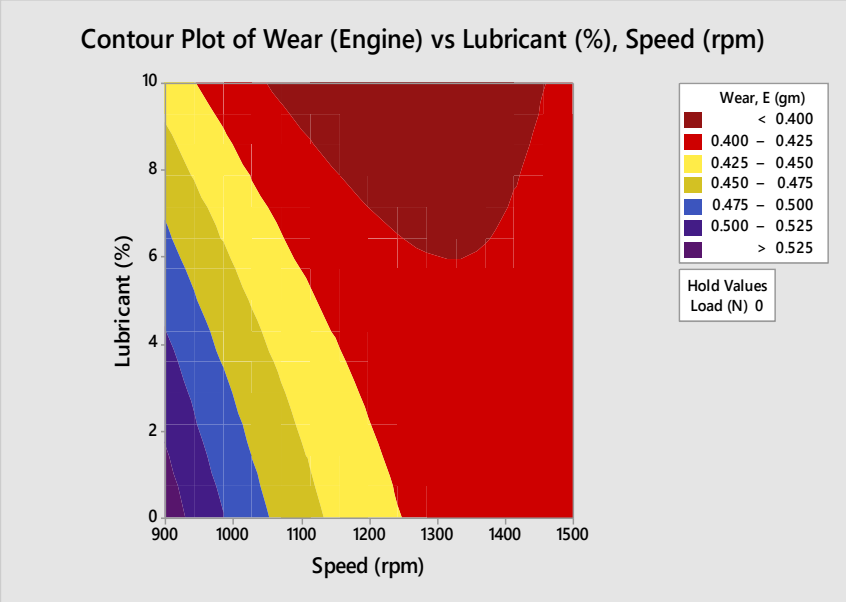
(a)


Surface Plot of Wear (Engine) vs Load (N), Lubricant (%)
Hold Values
Speed (rpm) 0
Wear (gm)
1.7
1.6
1.5
1.4
0
5
10
Lubricant (%)
200
150
100
Load (N)


Contour Plot of Wear (Engine) vs Load (N), Lubricant (%)
Load (N)
Lubricant (%)
200
180
160
140
120
100
0
2
4
6
8
10
Wear, E (gm)
< 1.45
1.45 – 1.50
1.50 – 1.55
1.55 – 1.60
1.60 – 1.65
1.65 – 1.70
> 1.70
Hold Values
Speed (rpm) 0

(b)


Surface Plot of Wear (Engine) vs Lubricant (%), Speed (rpm)
Hold Values
Load (N) 0
Wear (gm)
0.55
0.50
0.45
0.40
Speed (rpm)
1000
1200
1400
Lubricant (%)
0
5
10



(c)

Figure 4.17. Surface plot and contour plot for the effect of individual parameters on wear (engine) (a) load vs speed (b) load vs lubricant (c) speed vs lubricant.

4.5.4. Response optimizer and confirmation test

The main aim of the present investigation is to minimize the wear. To achieve this, optimization through RSM was carried out and resulted in the better combination in terms of blend ratio, load and sliding speed as shown in Table 4.5. Optimum factors are found to be blending of 10 % bio-lubricant in SAE20W40, sliding speed of 1293.93 rpm and load of 100 N as shown in Fig. 4.18. The value of wear (tribometer) and wear (engine) are 1.427 gm and 0.43 gm respectively at the optimised input parameters. The predicted value through RSM and experimental results are compared. The percentage error comes within the permissible range of 5 % [193]. Therefore, the equation of predicting value for wear (tribometer) and wear (engine) through RSM can be used to effectively estimate the wear (tribometer) and wear (engine) for any combination of lubricant, load and speed in the range of the conducted tests.

Table 4.5.

Optimization and confirmation test.

	Experimental results	**RSM predicted Responses**	**% Error**

Operating Conditions	Wear (Tribometer)	Wear (Engine)	Wear (Tribometer)	Wear (Engine)	Wear (Tribometer)	Wear (Engine)
Lubricant (10 %), Speed (1293.93 rpm), Load (100 N, 75%)	1.493	0.59	1.427	0.43	1.4	1.3

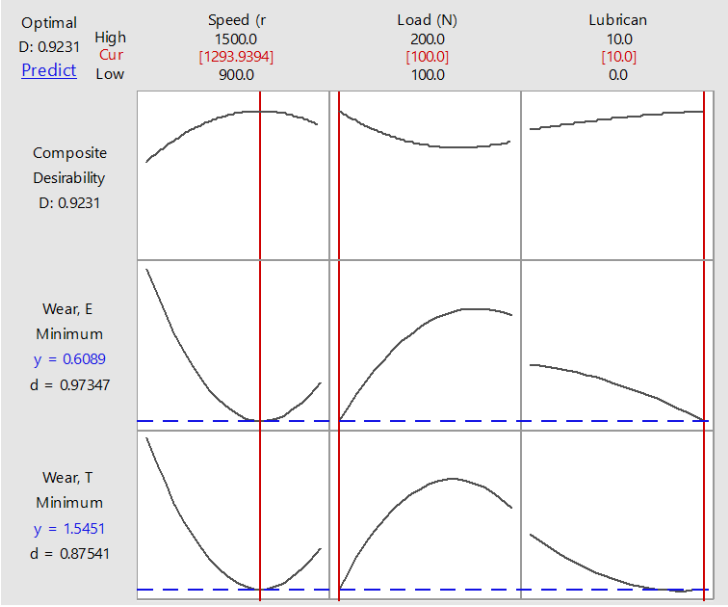


Figure 4.18. Optimization of wear (tribometer) and wear (engine).

4.6. Surface analysis with wear mechanism

There are various types of wear in the mechanical system, such as adhesive, abrasive, corrosive, and fatigue wear. The lubricant regime developed in this study was boundary lubrication therefore, adhesive, abrasive, corrosive and fatigue wear was observed on the surface during rolling mechanism [18, 77, 79, 82, 179, 192, 194-196]. However, the main wear mechanisms were abrasive and adhesive wear. The optical micrographs and

the SEM images of the tested Al-Si alloy pin under various types of bio-lubricants are shown in Figure 4.19 (a-g) and 4.20 (a-g). Fig. 4.19 shows the optical images of the worn surfaces and Fig 4.20 revealed the results obtained at speed 1500 rpm, load 200 N and different lubricants. The Fig. 4.20 (a-g-) represented the worn surface images taken through SEM with 3 D images of the pin. Referring to Fig. 4.19 (a-g) and 4.20 (a-g), it was found that the 5 and 10 % addition of chemically modified jatropha oil to the conventional lubricant shows minimum wear as compared to 5 and 10 % blend of pongamia oil and conventional lubricant. Improvement in the lubricant film thickness provides a protective layer which reduces the interaction of the surfaces in contact which leads to the minimum wear. With the comoparsion to the mineral oil, maximum surface damage was observed with 15% addition of the jatropha and pongamia blends.

Fig 20 (a) shows the SEM images for the base oil. More scratches on the surface have been observed and delamination of the surface was observed that was due to failure of the film on the surface. For chemically modified oil and concentration up to 10%, as depicted in Fig 20 (b-e), the absence of the delamination of the surface due to ploughing action was not visible there which results in the formation of the smooth surface. Although, some removal of the material is visible in magnified image, but it is comparatively very less. This was due to the presence of polyol esters in the structure which protects it by forming a protective film on the surface. The blends of the jatropha provides more effective lubrication due to the long molecular straight chain of the modified oil with comparison to the pongamia oil. Fig 20 (f-g) shows the effect of adhesion and abrasion on the surface when the amount in blend percentages increases upto 15%. This was due to the depletion of the additives from the base oil, breakage of the ester chain from the molecular structure and oxidation of more amount of metals from the surface.

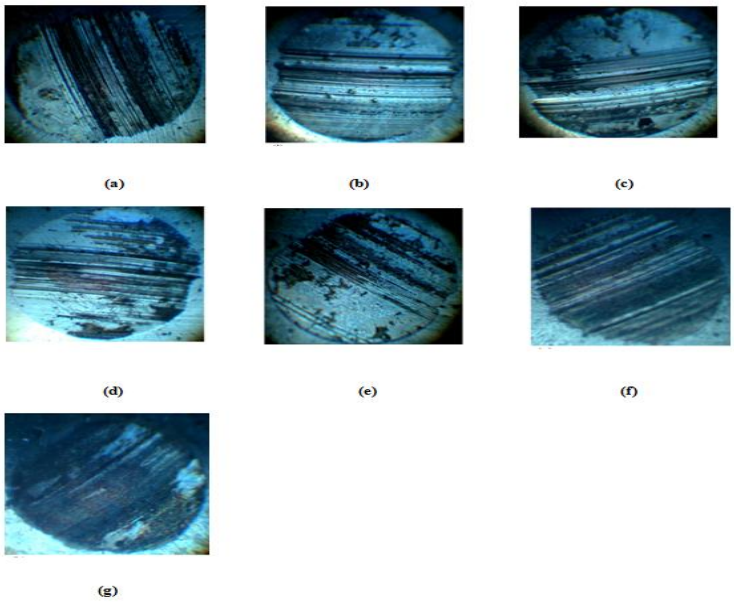
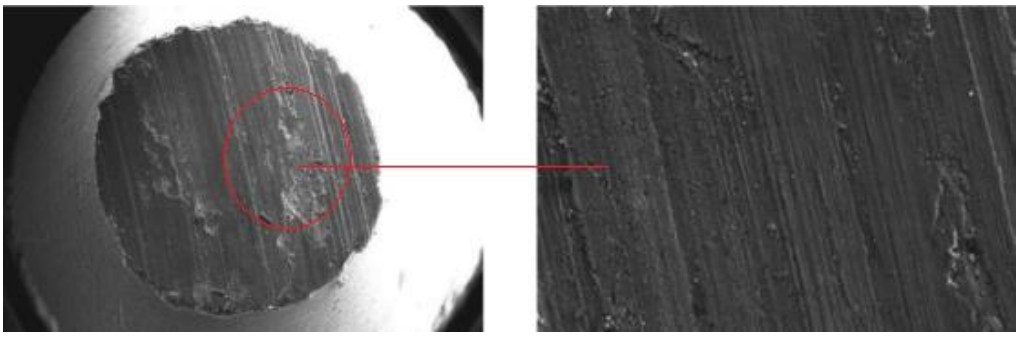
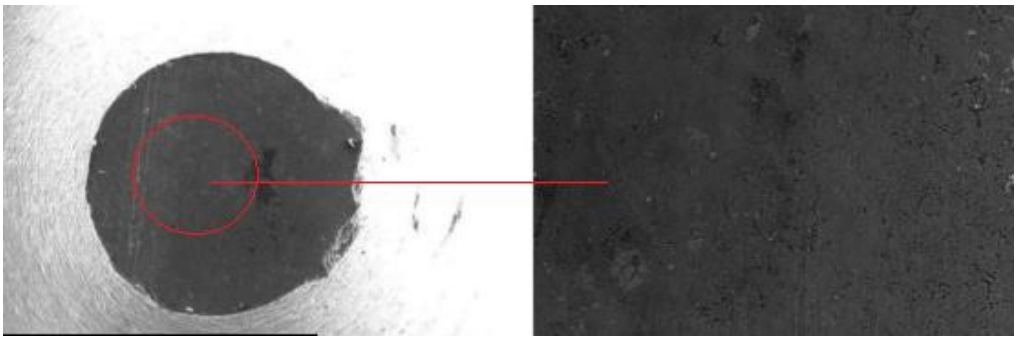


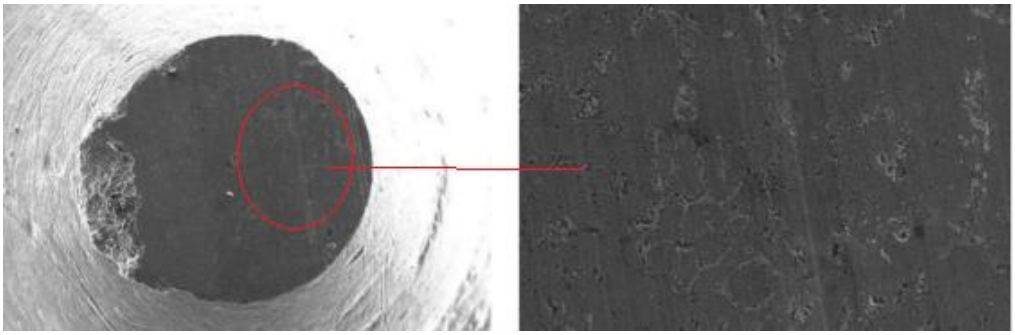
Figure 4.19. Optical micrographs showing wear scars for (a) M100 (b) JB 5 (c) PB 5 (d) JB 10 (e) PB 10 (f) JB 15 (g) PB 15.



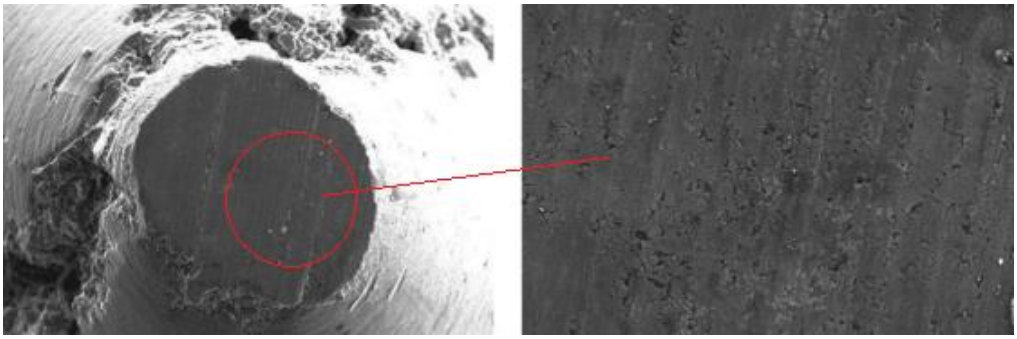
(a)



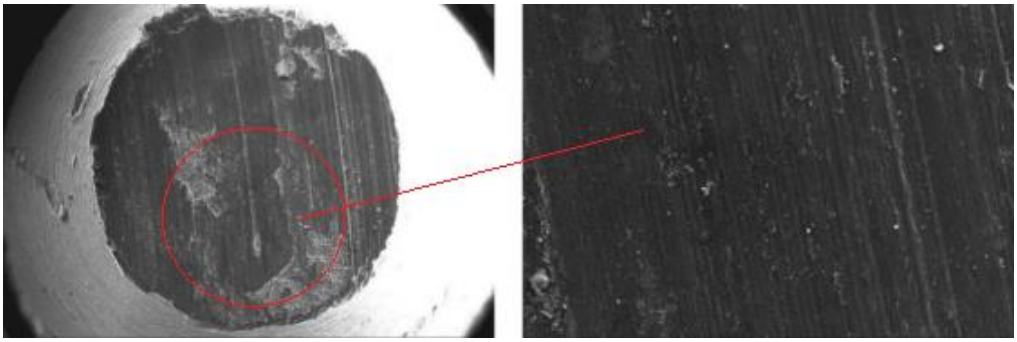
(b)



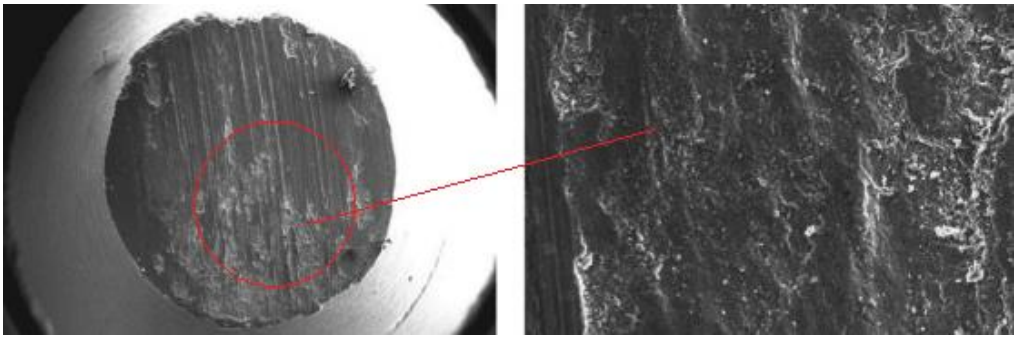
(c)



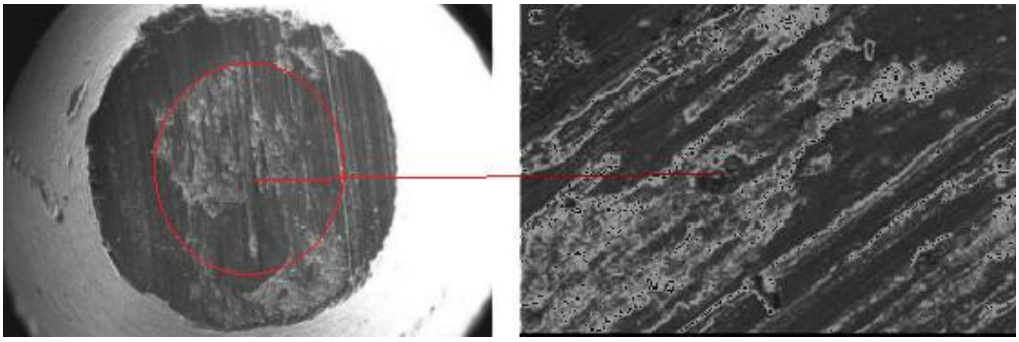
(d)



(e)



(f)



(g)

Figure 4.20. SEM images and 3D worn surface of the pin with different lubricants (a) M100 (b) JB 5 (c) PB 5 (d) JB 10 (e) PB 10 (f) JB 15 (g) PB 15.

4.7. Discussions

In general, chemical modified non-edible oil-based lubricants contain better lubricity than the petroleum-based lubricants during boundary lubrication regime which has already been stated in the previously published literature [197]. The presence of fatty acid molecules inside the non-edible vegetable oils contributes in forming low shear strength metallic soap while reacting with the metallic surfaces. The reaction of the stearic acid present in fatty acids molecules with the iron present in the metal results in the formation of an iron stearate protective layer on the surface. The formation of the soap layer significantly reduces the COF and wear from the surface during all applied conditions. The anti-wear and lubricity properties of the oil increase with the presence of long-chain fatty acid molecules despite short-chain fatty acids. The non-edible vegetable oils containing a higher amount of oleic acid (C18:1) have the capability to sustain the degradation of the protective layer formed between the surface in contact thus reducing COF and it increases the density of the fatty acid monolayer resulting in effectively reducing the wear during operation [198].

However, some studies have also reported an increase in wear while using bio-based lubricants. The removal of the metallic soap layer occurred during continuous sliding motion. So, maximum wear was observed at low sliding speed due to the time available for the continuous removal of the layer. The reformation of the layer occurs again and again by the chemical reactions occurred on the surface. The corrosive effect of peroxide and free fatty acids

leads to oxidation which contributed to an increase in wear [199]. The increase in the amount of trimethylolpropane (TMP) after a certain amount results in more wear as discussed by Zulkifli et al. [190]. It was stated that the bio-based lubricant can easily oxidize at an elevated temperature while leaving a corrosive layer on the surface. In their subsequent study, jatropha oil-based TMP provides a better load-bearing capacity compared to the liquid paraffin. So, the tendency to maintain a sustainable lubricant layer is attributed more to the Jatropha oil TMP. However, based on the conditions applied, there is also a need for some additives to increase the efficiency lubricity property of the lubricant [200].

Chemically modified non-edible oils are superior during the tribological analysis with comparison to the natural non-edible oils as they contain more viscosity which contributes to enabling the process of formation of a protective layer between the surfaces. The chemical modified non-edible oils don't get oxidized easily as compared to the without modification non-edible oils which contributed to reducing the wear by forming less oxidative products. Adhvaryu et al. [201] stated that the chemically modified soyabean oil revealed less coefficient of friction than the raw soyabean oil. It was discussed that the physical and chemical interactions that polar functional groups in the triacylglycerol molecule make physical and chemical interaction with the metallic surfaces under high load and sliding contact. Therefore, the increase of the polar functionality in vegetable oil structure through chemical modification has a positive impact on lubricity [202].

CHAPTER 5
CONCLUSIONS AND SUGGESTIONS

This chapter presented the outcomes obtained from the study and they are correlated with the objectives defined in chapter 1. The findings are summarized point by point while keeping the objectives in line with relation to the aim of this study. Future work recommendations, publications obtained from this work, and the scientific knowledge obtained are also mentioned in this chapter.

5.1. Achievement on objective 1

Physicochemical analysis of the bio-based lubricant properties was necessary to understand as they are responsible for the changes occurred when operated at different conditions. The properties of the chemically modified lubricant up to 10% mixing for both the oils were found to be significant during their application while using them as an alternative to the mineral oil. The 15 % addition of the bio-based lubricant to the reference oil didn't contributed in obtaining better results with comparison to the mineral oil.

5.2. Achievement on objective 2

The friction and wear behaviour of the chemically modified jatropha and pongamia oil imparts effective contribution during their analysis. The 5% and 10% addition of both the oils results in reduction of COF, wear, wear scar diameter and improved surface was obtained during the sliding motion. The 15% addition of the chemically modified oil contributed towards an increment in friction and wear of the material in reference to the mineral oil. The 15% blends shows the maximum degradation of the lubricity properties due to the presence of more amount of acidic content. The maximum COF and wear was obtained at higher load and minimum sliding speed during all the conditions applied.

In view of this, significant improvement in the properties of the bio-lubricant are required to address and it can replace mineral oil during several applications. This can be achieved with the proper usage of the additives like anti-wear, extreme pressure, nanoparticles and can evaluate their performance during different conditions.

5.3. Achievement on objective 3

To correlate the parameters used during the tribological analysis with real engine, Response Surface Methodology approach was utilized. The performance of the chemically modified non-edible oils (jatropha and pongamia) was assessed on POD tribomeetr to analyze their friction and wear behaviour for the attempt to get the best lubricant blends. The 5 % and 10 % bio-lubricant blends comes out as best blends which further utilized to compare their performance with real operating diesel engine conditions. Response surface methodology technique provided the optimum results in which 10 % blend performed well at all operating conditions.

In view of this, significant further work should be conducted to check their behaviour during long term endurance testing on diesel engine. A key investigation should be to add some oxidizers and additives to the non-edible vegetable oil and assess its successive performance.

5.4. Achievement on project aim

Overall, the analysis of the modified bio-based lubricant provides an improved results by reducing the friction and wear behaviour between the sliding surfaces during their contact and indicates that they are sustainable during their usage in practical applications (e.g. automotive engines, industrial machines etc.). However, some of the points are needed to address to make them technically and commercially feasible. There are two pints which needs to give priority while addressing there limitations i.e. improvement in the oxidation stability and anti-wear characteristics.

5.5. Contribution to scientific knowledge

The application of chemically modified jatropha and pongamia oil proves to be a promising approach during their implementation as an alternate to the mineral oil. The outcome of the bio-based lubricant during their tribological analysis on pin on disc tribometer provided an improvement during sliding contact under different operating conditions. The scientific knowledge obtained from this study are:

- During the sliding motion between the surfaces in contact, the considered parameters load, speed and lubricant influenced effectively their friction and wear characteristics. Higher load, lower speed and up

to 10% bio-lubricant application adversely affected the tribological performance of the surfaces in contact. Better results are obtained during the application of 5 % and 10 % blends for all conditions considered during the tribological analysis.

- In terms of wear, increased sliding speed results in minimum wear of the surfaces. Much more reduction in the wear of the material was observed at lower loads due to the presence of hydrodynamic lubrication regime.
- The wear occurred during the sliding motion when surfaces are in contact follows the Archards adhesive wear law while considering the application of the applied loads. It can be stated that maximum amount of stress is produced when load is increased on the surface of the lubricant film.
- The acidity in the lubricant after test is more at higher loads due to oxidation of the material from the surfaces in sliding contact. All the bio-lubricant blends showed improved results as compared to mineral oil except 15 % blends at all operating conditions du to the presence of more acidic content.
- During correlation of the POD machine and engine parameters, the wear obtained while considering the tribometer machine are very similar to the wear obtained during the performance on the diesel engine test rig. The concept of the oiling mechanism differs while considering POD tribometer and the diesel engine test rig. Fresh lubricant supply is maintained during the supply of lubricant to the POD machine after every conditions prevailed during the analysis. However, this doesn't affect the analysis while considering the certain conditions prescribed during evaluation on each .machines. It stated that the sliding speed, load, and lubricant are the crucial parameters considered during the analysis for getting a susceptible model which could correlate conditions prevailed on the POD machine and diesel engine.
- Results of ANOVA analysis discovered that:

(i) The developed regression analysis based model of wear (tribometer) and wear (engine) are quite significant containing around 99% confidence interval.

(ii) In the case of wear (tribometer), the influence of lubricant is more followed by the load while in the case of wear (engine), again lubricant influenced more followed by the sliding speed.

- From the response surface plots, it can be determined that the maximum wear was detected at higher load and lower speed. Ratio of 5 % and 10 % blends showed better results in terms of reducing wear at all operating conditions.
- Based on the optimization process while reducing wear, $A_3B_1C_3$ showed optimum combination and its composite desirability comes out 0.969 which is almost nearer to the value 1.
- During the confirmation test to validate the models developed using RSM were found to be in considerable. The developed models indicated that they are capable and sufficient enough to describe the efficiency of the sliding speed, load and lubricant ratio on the wear characteristics of the metal surfaces in contact during tribological analysis and the error predicted was found to be within 10 % limit.

5.6. Future work recommendations

The results of this work provides a substantial input to the lubricant industry while considering bio-based lubricant as an alternative to the mineral oil during their tribology characterization. The development of the bio-based lubricant provided a significant improvement while reducing friction and wear characteristics of the surfaces during their sliding motion.

The application of the bio-based lubricant utilized in this study is limited to the conditions which are mentioned during the present study. So, further improvement is needed while considering bio-based lubricant for the tribological analysis and to make them feasible on a large scale.

To make the bio-based lubricant alternative to the available mineral oil, improvement in the certain properties in needed. These are related to their oxidation stability at a higher temperature and the degradation of the properties with further blending of the chemically modified oils. These properties can be

improved by utilizing certain additives which are commercially available. These are anti-wear additives, extreme pressure additives, and anti-friction additives and nowadays, more studies are focussing on the utilization of the nano-additives to improve their lubricity properties. So, the further study can be conducted by considering these parameters as a property improvement additives so that an environmental-friendly lubricant could be provided to the community.

5.7. Publications obtained from this work

5.7.1 Peer-reviewed journal

1. **Yashvir Singh**, Rajnish Garg, Suresh Kumar. 2016. “Effect of load on friction and wear characteristics of Jatropha oil biolubricat” published in Biofuels (taylor and francis publications). Vol. 8, 1, 125-133. DOI: https://doi.org/10.1080/17597269.2016.1215065.

   (SCI Indexed)

2. **Yashvir Singh**, Rajnsih Garg, Suresh Kumar. 2016. "Comparative tribological investigation on EN 31 with pongamia and jatropha as lubricant additives" published in Energy sources part a. recovery, utilization and environmental effects (taylor and francis publications). Vol. 38, 18, 2756-2762.

   (SCI Indexed)

3. **Yashvir Singh**, Rajnish Garg, Ajay Kumar. 2016."Tribological behavior of pongamia oil as a lubricant additive" published in Energy sources part a. recovery, utilization and environmental effects (taylor and francis publications). Vol. 38, 16, 2406-2412.

   (SCI Indexed)

4. **Yashvir Singh**, Rajnish Garg, Suresh Kumar. 2015. "Aspects of non-edible vegetable oil-based biolubricant in the Automotive Sector" published in Green- a systematic approach to energy (Walter De Gruyter), Vol . 5, 1-6, 59-72. DOI:10.1515/green-2015-0003.

   (SCOPUS Indexed)

5. **Yashvir Singh,** Rajnish Garg, Suresh Kumar. 2015. "Optimization of tribological behavior of Pongamia oil blends as an engine lubricant

additive" published in Green Processing and Synthesis (Walter De Gruyter), Vol. 4, 5, 421-431.DOI: 10.1515/gps-2015-0056.

(SCI Indexed)

6. **Yashvir Singh,** Rajnish Garg, Suresh Kumar. 2019. "Effect of sliding speed and temperature on the tribological behaviour of pongamia oil based blended lubricant" published in Energy sources part a. recovery, utilization and environmental effects (taylor and francis publications), vol. 41, 4, 468-480.

(SCI Indexed)

7. **Yashvir Singh,** Rajnish Garg. 2019. **"**Development of Bio-Based Lubricant from Modified Pongamia Oil (Pongamia Pinnata) and Their Tribological Analysis" communicated and under review to Energy sources part a. recovery, utilization and environmental effects (taylor and francis publications) on 24-5-2019.

(SCI Indexed)

8. **Yashvir Singh**, Rajnish Garg. 2019. **"**Friction and Wear Characterization of Modified Jatropha Oil (Jatropha Curcas) using Pin-on Disc Tribometer" communicated and under review to Energy sources part a. recovery, utilization and environmental effects (taylor and francis publications) on 27-5-2019.

(SCI Indexed)

5.7.2. International Conference

1. **Yashvir Singh**, Rajnish Garg, and Suresh Kumar. "Friction and wear characterization of the jatropha oil based biolubricant" presented in *3rd National Conference on Recent Advances in Sciences & Technology* during 11-12 November, 2017 at Semant Institute of Technology, Pithoragarh, Uttarakhand, India.
2. **Yashvir Singh**, Rajnish Garg, and Suresh Kumar. "Experimental analysis of the modified pongamai oil for the tribological characterization" presented in *3rd National Conference on Recent Advances in Sciences & Technology* during 11-12 November, 2017 at Semant Institute of Technology, Pithoragarh, Uttarakhand, India.

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