

**TRIBOLOGICAL STUDY OF DIRECT INJECTION DIESEL
ENGINE FUELLED WITH DIESEL BUTANOL BLENDS**

**A thesis submitted to the
*University of Petroleum and Energy Studies***

**For the Award of
Doctor of Philosophy
in
Mechanical Engineering**

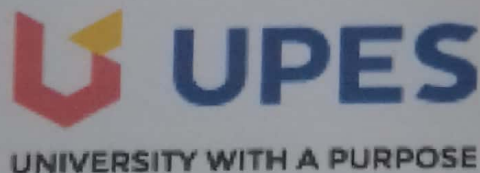
**By
Santosh Kumar Kurre
(SAP ID 500014051)**

December 2018

Internal Supervisor(s)

**Dr. Rajnish Garg
Professor
Department of Mechanical Engineering
University of Petroleum & Energy Studies**

**Dr. Shyam Pandey
Professor
Department of Mechanical Engineering
University of Petroleum & Energy Studies**

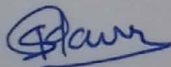


**Department of Mechanical Engineering
School of Engineering
University of Petroleum & Energy Studies
Dehradun-248007: Uttarakhand**

October 2019

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I declare that the thesis entitled “Tribological Study of Direct Injection Diesel Engine Fuelled with Diesel Butanol Blends”, has been prepared by me under the guidance of Dr. Rajnish Garg, Professor in Mechanical Engineering Department, and Dr. Shyam Pandey, Professor in Mechanical Engineering Department, University of Petroleum & Energy Studies. No part of this thesis has formed the basis for the award of any degree or fellowship previously.



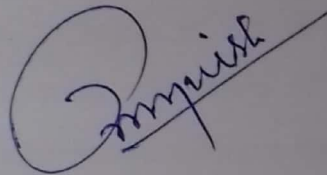
Santosh Kumar Kurre
SAP ID- 500014051

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We certify that Santosh Kumar Kurre has prepared his thesis entitled “Tribological Study of Direct Injection Diesel Engine Fuelled with Diesel Butanol Blends”, for the award of PhD degree of the University of Petroleum & Energy Studies, under our guidance. He has carried out the work at the Department of Mechanical Engineering, University of Petroleum & Energy Studies.

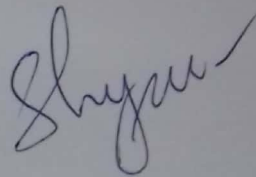
Internal Supervisor(s)

Dr. Rajnish Garg



Professor,
Department of Mechanical Engineering
University of Petroleum & Energy Studies
Dehradun

Date:



Dr. Shyam Pandey

Professor,
Department of Mechanical Engineering
University of Petroleum & Energy Studies
Dehradun

Date:

DECLARATION

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SAP ID: 500014051

Date: _____

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Dr. Rajnish Garg
Internal Guide
Professor
UPES, Dehradun

Dr. Shyam Pandey
Internal Co-Guide
Professor
UPES, Dehradun

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Abstract

Gradual depletion of petroleum reserves and the stringent norms of exhaust emission has led to search for a suitable alternative fuel for diesel engines. The oxygenated fuel like, ethanol, methanol and butanol may be promising fuel for diesel engines. Butanol has several advantages over ethanol, including enhanced tolerance to water contamination allowing the use of existing distribution pipelines, the ability to blend at higher concentrations without retrofitting vehicles, and better fuel economy.

Chapter 1 describes the necessity and motivation for the tribological study of diesel engine to assess the condition of engine oil in order to maintain the engine properly when engine is fueled with the butanol blended diesel fuel and setting the objectives of the study.

Chapter 2 contains a very exhaustive review of the existing literature on the feasibility of the possible biomasses (oil) to be used as biofuel or alternative fuel for the diesel engines. The comparative study among various biofuels has revealed that the higher alcohol (butanol) also has the potential to be used as biofuel and as a blend with diesel. It has significant properties such as enhanced tolerance to water contamination allowing the use of existing distribution pipelines, the ability to blend at higher concentrations without retrofitting vehicles, and better fuel economy which differ from other fuel stock and make it best choice for the diesel engine fuel. This chapter also describes the lubricant condition monitoring for different diesel engines fueled with biofuels and their blends. The engine oil gets contaminated due to the biofuels and the life of oil is reduced. Once the engine oil gets depleted due to soot formation, fuel dilution, moisture or water and thermal oxidation of the engine oil when used for long time, the wear of engine components increases. The properties of engine oil change with the time and with use of biofuels. The degradation of the engine oil results in the formation of oxides, decrease in viscosity, decrease in TBN and increase in TAN. After the exhaustive literature review, the gaps were identified and the objectives of this work were set.

Chapter 3 covers the lubrication principle, lubricant properties and degradation of the engine oil. The function of engine oil in the engine is very important for the smooth running of engine as it plays many roles in the engine. Lubrication is attained by evolving the physical and chemical characteristics of the lubricant. Physical properties such as density, viscosity, heat capacity, thermal conductivity, and the temperature- pressure- viscosity relationships decide the working capacity of the lubricant under the hydrodynamic lubrication. Engine oil is used to reduce the friction between the mating surfaces, provide lubrication, reduce engine component wear, provide sealing, provide cooling against thermal exposure, ensure cleaning for better movement of internal components of the engine and neutralize the corrosive effect of the acids.

Chapter 4 describes the experimental procedures and test methods for endurance testing of engine and measurement of physico-chemical properties of fresh and used blends through engine oil analysis. The study of tribological aspects of butanol-fueled engine is very essential from lubrication and choice of lubricant point of view. The condition of lubricant in engine gives significant information of wear in engine components and needs to be studied for the endurance and durability of the engine operation with diesel butanol blends. However, if the new fuel is introduced or new concept in the engine design is implemented then there is a significant challenge for engine oil condition.

Three fuel blends of different proportion of butanol and diesel were prepared on volume-to-volume basis. The blends were termed B10 containing 10% butanol, B15 containing 15% butanol, and B20 containing 20% butanol. Though, butanol is miscible in the diesel, the additive (hydrofuran) was added to get the homogenous blend while biodiesel was used as a co-solvent to get the stable blends and to maintain the cetane number of the blends. The experimental set up consists of a Kirloskar make, 5 HP, 4 stroke single cylinder, water cooled diesel engine with loading conditions as per IS:10000. There were four identical engines installed at a common place in order to maintain the same atmospheric/ environment test conditions. All the engines were operated at a constant speed of 1500 rpm. As per IS:10000 code, to

perform an endurance test, engine needs to run to 32 cycles, each cycle comprised of 16 hours of continuous run. The engine runs initially for 30 minute to warm up the engine and maintain the constant speed. After warm up period, the engine is subjected to 100% rated load to replicate the harsh driving condition. Subsequently, it is loaded 50% rated load (moderate load condition) and 110% rated load to replicate severe loading followed by running at no load condition for 30 minutes. At the end of 16 hours cycle, the engine was stopped for necessary servicing and adjustments. The engine oil samples were collected carefully from the engine sump after completion of every 48 hours of run using syringe. The samples were stored in the cool and dry place to keep it safe from the contamination until it was prepared for the Atomic absorption spectroscopy (AAS) analysis. These samples were converted into the aqueous solution of 100 ml and subjected to wear particle analysis in the atomic absorption spectroscopy within the 24 hour of sampling. The complete characterization of used lube oil was carried out through a set of the different analysis such as TBN, TAN, viscosity, density and wear metals content.

Chapter 5 elaborates the results of the tests followed by discussion. Engine oil analysis of all the engines shows increasing wear with the usage time and increasing butanol content in the blends as compared to the diesel fuel. The viscosity of the engine oil from all four engines initially decreases in the running in period of 144 hour of engine run. The viscosity of engine oil of diesel-fueled engine reaches its limiting point within 96 hours of run while that of B10 and B20 fueled engine oil reaches between 144-196 hours of run. Total base number decreases with the usage time while total acid number increases. The total base number of the all the engine oil samples reaches to its limiting value between the 288-336 hours of run. The total acid number of engine oil from B10, and B15 fueled engine reaches the limiting value after 288 hours. The density of engine oil initially decreases but then increases for all the engine oil samples. The results reveal that the wear in blended fueled engine is higher than the diesel fueled engine. The iron wear is higher than the copper wear due the less contributing copper components in the engine.

Engine oil degrades because of the contamination, which occurs due to wear metals, fuel dilution, oxidation, external particle ingress and blow-by gases containing the unburned butanol and biodiesel. Butanol increases the oxidation of the engine oil by contributing more oxygen.

This chapter also describes the visual inspection of the engine component such as piston, piston ring, and cylinder. The mass loss of the cylinder of B15 fueled engine is higher than the diesel and B10 fueled engine. The total mass of the piston rings was found higher for the B10, and B15 fueled engine than the diesel-fueled engine, which is an agreement to higher concentration of the iron and copper in the engine oil of B10, and B15 fueled engine than that of diesel-fueled engine. However, the B20 fueled engine is found to have broken piston, piston ring and bearing after the test. All the results are discussed thoroughly with suitable reasons to support the observed trend/behavior.

The drain period of engine oil is dependent on different parameters of engine oil and visual inspection of the engine components. The dominant parameters are viscosity, TAN, TBN and wear. Based on all result of the engine oil analysis and visual inspection, a drain period of 100 hours is suggested for engine oil of B10 and B15 fueled engine.

Chapter 6 consists the conclusion drawn from the present work and future scope of this work. There is no operational problem with diesel- butanol blends up to the 15% of butanol. However, the higher percentage of butanol creates durability problems. Finally, it is concluded that butanol has potential to be used as a blend with diesel without any modification in existing diesel engines.

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CHAPTER 1: INTRODUCTION

1.1 Problem definition

1.1.1 Background

Gradual depletion of petroleum reserves and the stringent norms of exhaust emission lead to search for a suitable alternative fuel for diesel engine. It is particularly basic to utilize alternative fuel because of environmental concerns, socio-economic issues, energy security, and foreign exchange savings. Most of the country in the world started production of the biofuels since biofuels have enormous benefits over the petroleum fuels. The production of biofuels has exponentially increased from last two decades. Several countries have set their biofuel production target such as, Renewable Fuel Standard (RSF) of the United States has targeted 7.5×10^9 gallons of renewable fuel to be blended with the transportation fuels by 2012, and 36×10^9 gallons by 2022. Similarly, the European Union (EU) Renewable Energy Directive (RED) has mandated a 10% renewable energy component in the transportation sectors of every EU member state by 2020 with 7% from biofuels and 3% from vehicle electrification [1]. In France, the blending of biodiesel and diesel is allowed up to B30 and the blending of ethanol and diesel is allowed up to E10. While the well-developed market for the bioethanol is hold up by Brazil and the USA, the blends up to E25 can be obtained [2]. Average energy consumption in the transportation sector is advanced by 1.1% per year because of vehicles and industrial applications worldwide. Hence, there is a huge requirement of the fuel to be used in place of diesel. Biofuels are having the potential of to replace the diesel fuel. Rudolf Diesel, the inventor of compression ignition engine had started using peanut oil as a fuel in the diesel engine at its early stages. Vegetable oils, whether edible or non-edible can be used as a biofuel in the engine. Several researchers have tested the variety of vegetable oils as fuel

and found that it has the potential to be used as a fuel. However, they have experienced the number of problem such as, injectors choking which leads to poor fuel atomization, poor combustion and lubricating oil thickening. [3] Many efforts have been reported in literature where the use of renewable gaseous and liquid fuels is recommended for the diesel engine by researchers and scientists. The oxygenated fuels like, ethanol, methanol and butanol may be promising fuel for diesel engine. The butanol (higher alcohol) also has the potential to be used as biofuel and it can be blended with diesel. It has many significant properties such as increased tolerance to water contamination permitting the employment of existing distribution pipelines, the power to mix at higher concentrations while not retrofitting the vehicles, and higher fuel economy. The study of tribological aspects of butanol fueled engine is very essential from lubrication and choice of lubricant point of view. The condition of lubricant in engine gives the significant information of wear in engine components and needs to be studied for the endurance and durability of the engine during operation with diesel butanol blends. However, if the new fuel or new concept in the engine design is introduced than there is a significant challenge for engine oil condition. When biodiesel comes into the contact of engine oil, it accelerates the oxidation of oil and also accumulates the fuel. The by-products of oxidation of oil form the oil insoluble and acid. The viscosity of oil is increased significantly due to insoluble. Use of ethanol in the engine causes the lowering of engine cylinder temperature due to slow evaporation low cetane number of ethanol. Also, ethanol possesses hygroscopic property and acids which forms the stable emulsion in the engine oil. Oxidation of the engine oil is accelerated by utilization of ethanol in the engine very similar to the biodiesel. In the present scenario, reduction in generation of greenhouse gases by transport vehicle is the challenge for engine manufacture as well as for the reliability of engine oil. The main aim is therefore to estimate the wear, the engine oil degradation and oil drain period of the bio fueled (butanol) engine.

1.1.2 Need for research

Diesel-butanol blends are more promising than the diesel-ethanol blends because it has many advantages. Butanol has higher heat content and high miscibility property in diesel than ethanol. The vapor pressure of butanol is much lower than that of ethanol. The solubility property of the alcohol mainly depends upon the carbon chain length of the alcohol. Butanol can be blended with diesel oil in any proportion. It does not detach once mixed with diesel even in cold conditions. Butanol reduces the solidification temperature of the fuel in cold condition. The low cetane number of butanol is main obstacle to blend with diesel. When mixed with diesel, it diminishes the auto ignition temperature of the fuel blends at the time of combustion henceforth, to overcome that problem some CN improver is required.

In comparison, the suitability of butanol and ethanol for diesel engine fuel, butanol is far better than ethanol as an alternative fuel. Butanol possesses higher energy density, less corrosive, more resistant to water contamination, higher cetane number and higher blending stability in comparison to ethanol. Higher production cost of butanol than ethanol is the only disadvantage of butanol [4]. Although the longer-chain alcohols are more appropriate for making blends with diesel, the properties such as viscosity, cetane rating, and lubricity of butanol-diesel blends still require some improvement. The mixing of biodiesel in the diesel- butanol blends can improve these properties [4].

The higher oxygen content in n-butanol reduces more soot as compared to biodiesel. The viscosity of n-butanol is nearly equal to that of diesel, while the viscosity of the diesel is lower than that of biodiesel. Thus n-butanol is more suitable for diesel engine [5]. Various researcher have tested the engine with different blends of alcohol- diesel and alcohol- gasoline, diesel- biodiesel, or straight vegetable oil from both edible and non-edible seeds. The common problem with the SVO fueled engine is lowering of the lubricating oil viscosity, chromium built up in lubricating oil, decrease in oxidation stability, base number, wear of injection system, fuel pump wear, fuel valve wear and compression ring wear. Further, the biodiesel and their blended fueled engine experience higher iron concentration in the lubricating oil for safflower base biodiesel, contamination of lubricating oil, moving part sticking, injector

choking, filter plugging, ash content and carbon deposit in combustion chamber while alcohol blended fueled engine experiences higher bore wear, increased oil consumption, loss of performance, wear of fuel injector, wear of valve seat material, sticking fuel injector, piston ring wear and pump damage because of corrosion. Emission and performance analysis on the short term test of diesel engine fueled with blends of butanol and diesel is reported by many researchers. But, it is very necessary to examine the engine for long duration to know the engine durability with this fuel, oil deterioration and its mechanism. The engine lubricating oil analysis is a very powerful tool to analyze the engine health and wear of the engine components. Very few studies have been conducted on wear of engine components with butanol blended fuel specifically with the diesel- butanol blended fuel. Engine lubricating oil analysis gives an idea about the present and future states of the engine and the components as the property of engine oil changes with different operating conditions and thermal environment. Engine oil deteriorates with the time because of wear of engine component, contamination, dirt etc. So, the durability test of diesel engine fueled with the diesel- butanol blend need to be performed to know the wear of the engine components and degradation in the properties of engine oil.

1.1.3 Objectives

1. Study of the physio-chemical properties of the lubricating oil for the engine fueled with diesel- butanol blends.
2. Study of the lubricating oil performance with reference to engine component wear and quantification of the wear in diesel- butanol blend fueled engine.
3. To understand the attributes to the lubricating oil deterioration with the use of diesel- butanol blends.
4. Develop an approach for the lubricating oil drain interval for the engine using diesel- butanol blends.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The global energy crises, exhaustion of fossil fuels, deficient resources of petroleum and inflexible administration norms have compelled the researchers to search the alternative fuels for diesel engine. The early research on alternative fuels included vegetable oils such as Jatropha, palm, sunflower, rapeseed, and soy bean oil. N. Tippayawong et al [6] examined performance and emission of diesel engine fueled by neat palm oil and neat soybean oil separately and found that the vegetable oil fueled engine performs and produces similar emission as diesel fueled engine. The higher viscosity of vegetable oil causes problem in fuel injection and pre-heated oil produced more NO_x emission than the unheated. Syndi L. Nettles-Anderson et al [7] reported in a review paper that straight vegetable oil having high value of fully saturated fatty acid has the ability to decrease the NO_x emission. However, it increases the viscosity and cloud point. Polyunsaturated fatty acid also results in cylinder buildup. The utilization of vegetable oil in the diesel engine leads to carbon deposits in cylinder and piston, engine durability problems and engine oil contamination. Because of such problems with vegetable oil, there is a need of conversion of the vegetable oil in to the biodiesel. Biodiesel can be formed by the transesterification of vegetable oil or animal fats. Biodiesel encompasses fatty acid methyl ester (FAME) [8]. Several researchers calculated the performance, emission and wear of compression ignition engine with the biodiesel fuel. The brake specific fuel consumption (BSFC) was found to increase and brake thermal efficiency was found to decrease with biodiesel. Since biodiesel has lower calorific value than diesel fuel, more fuel is required to produce same energy for given amount of fuel. However, the emission such as carbon dioxide (CO₂), particulate matter (PM), hydrocarbon (HC) got reduced. The biodiesel is also used as the lubricity provider for the diesel engine. Commercial biodiesel in low sulfur diesel enhances the lubricity more than neat fatty esters [9]. The lubrication property of biodiesel makes it a suitable additive for lubricity enhancer in petroleum fuel [10]. However, the

blend of unstable biodiesel and diesel may produce engine deposits, ring bulging and thickening of lubricating oil etc. when used for long time run [11]. Biodiesel improves the lubricity property by making the film on the surface of the mating parts and prevents the contact between two components having relative motion [12]. The properties of some vegetable oil are enlisted in the Table 2.1[6, 13-21].

Table 2-1: Properties of biofuels and diesel [6, 13-21]

| Biofuels | Calorific value Mj/kg | Density g/cm ³ | Kinematic viscosity (cSt) | Flash point K | Sulphur % mass | Moisture % volume | Cetane number |
|---------------|--------------------------|------------------------------|---------------------------------|---------------------|-------------------|----------------------|------------------|
| Diesel | 42.5 | 0.871 | 2.4 | 344 | | | 52 |
| Jatropha | 38.2 | 0.932 | 52.2 | 483 | - | - | 38 |
| Sunflower oil | 39.5 | 0.918 | 58.5 | - | - | - | 37.1 |
| Palm oil | 38.0 | 0.918 | 42 | 446 | | 0.02 | 43 |
| Soybean oil | 37.9 | 0.915 | 41.2 | 458 | | | - |
| Rapeseed oil | 37.1 | 0.85 | 8 | 593 | - | - | |
| Coconut oil | 37.26 | 0.93 | - | - | 0.009 | - | 37 |
| Biodiesel | 40.5 | 0.855 | 4.57 | 399 | | | 52 |
| Methanol | 19.7 | 0.792 | 0.59 | 284 | | | <5 |
| Ethanol | 26.8 | 0.794 | 1.1 | 286 | | | 6 |
| Butanol | 33.1 | 0.810 | 2.63 | 308 | | | 25 |

Evangelos G.G.et al [22] reported the beneficial effect of utilizing the blends of diesel and n-butanol on CO emission and smoke at the expense of HC and higher NOx at different loads. 1- Butanol has been recently proposed to be used with gasoline [23]. Butanol possesses more corrosion resistant property than that of lower molecular alcohols such as ethanol and methanol. The phase separation does not occur in the blends of Butanol and diesel, blended in any ratio [24]. Rakopoulos et al [25] performed a test on the turbo-charged compression ignition engine to evaluate the engine performance and emission.

They supplied the blends of diesel- n-butanol and biodiesel and reported that the n-butanol blends reduce exhaust gas opacity significantly. Xiolei Gu et al. [26] examined the performance and emission of a low speed light duty diesel engine. They supplied different blends of Iso-butanol- diesel and normal butanol-diesel as fuel and reported that ignition delay with iso-butanol- diesel blends is lower than n-butanol diesel blends. The soot emission reduces substantially by adding butanol to diesel fuel whereas, the NO_x emission varies slightly.

A necati et al [27] performed an experiment on a six cylinder, turbocharged, direct injection compression ignition diesel engine to evaluate the emission and performance of the engine using blends of iso-butanol and diesel in diverse proportion such as 5%, 10% and 15%. They observed increase in brake specific fuel consumption and reduction in brake thermal efficiency with proportion of blends over conventional diesel fuel for low load conditions. They also found that the smoke opacity, NO_x, CO are reduced and unburned HC are increased slightly. Sehmas A. et. al [28] examined a mono cylinder compression ignition engine fueled with blends of biodiesel, butanol and diesel. They found an increase in brake specific fuel consumption (bsfc) and decrease in HC emission, CO and, brake thermal efficiency (Bth.) with blends over that with pure diesel. At low load, there is no significant change occurs in NO_x emission while at higher load, NO_x and smoke opacity reduces substantially.

Murat K et al. [29] examined the 4- stroke DI, compression ignition engine fueled with blends of diesel and iso-butanol. They operated the engine at the speed ranging between 1200 rpm to 2800 rpm, providing its full capacity. They found considerable decrease in brake power for blends having 15% and 20% iso-butanol but a slight decrease for 10% iso-butanol blend. They also found a decrease in NO_x and CO emission and increase in BSFC and unburnt HC with increasing iso-butanol content in the blend. Jikar et al [30] examined the 4- stroke 4- cylinder diesel engine fueled with methanol- diesel blends. They found lower exhaust gas temperature with blends of diesel –methanol than that of diesel. They reported an improvement in Brake thermal efficiency with blends over pure diesel but higher Specific Fuel Consumption as

compared to pure diesel. Alcohols are another promising biofuels which can be used in place of diesel fuel. Many exhaustive studies have been conducted to evaluate the emission and performance of diesel engine using alcohols such as methanol [31, 32], ethanol [18, 33-37] and butanol [28, 38-41] as a fuel either in pure form or blends with diesel since alcohols contain more oxygen and possess properties comparable to a fuel. Oxygen supplied by the alcohol helps in proper combustion. Butanol has good miscibility with diesel, higher energy density, better wear and corrosion properties and higher boiling point [42]. Therefore, it gives clean burning of fuel with less CO and smoke. K. Keerthi et al. [43] experimented on a compression ignition engine fueled with blends of biodiesel and diesel having 10% Iso-butanol as an additive. The brake thermal efficiency is found to increase with injection pressure till a pressure of 250 bar with slight increase in NO_x emissions and decrease in CO and smoke. Another study performed by Lennox Siwale et al [44] on turbo charged diesel engine fueled with the blends of diesel and butanol in varying concentration of 5%, 10% and 20% butanol at high load conditions and found that the addition of butanol decreases the regulated emission and soot formation due to the inbound oxygen atom of the hydroxyl group of n-butanol while HC increases because of slow vaporization and greater heat of vaporization of n-butanol blends. The other reason for rise in HC is ‘lean-outer-flame-zone’. The oxygenated fuel components increase the combustion efficiency and the premixed combustion becomes more intensive, causing an increase of NO_x emission [44]. D.C. Rakopoulos et al [38] have examined the mono cylinder, DI 4- stroke high speed compression ignition engine for performance and emission study. The engine was fueled with the blends of diesel and butanol in the proportion of 8%, 16% and 24% butanol and set to run at a constant speed of 2000 rpm. They observed a decrease in the NO_x, soot formation and CO emission but increase in HC, BSFC and Brake Thermal efficiency with increase in butanol content of the blends. Oguzhan Dogan [39] has examined the katana KM170 F mono cylinder, DI 4 stroke diesel engine fueled with blends of diesel and n-butanol having 5%, 10%, 15% and 20% butanol. He found that BSFC, HC and brake thermal efficiency increase with increase in butanol whereas NO_x, smoke, CO emission and exhaust gas temperature

decrease. Nadir Yilmaz et al [21] have examined Kubota, 6.5 kW 4- stroke, 2 - cylinder indirect injection engine fueled with biodiesel –butanol blends having 5%, 10%, and 20% butanol and found increase in NO_x and decrease in CO emission for low butanol contents whereas NO_x and HC decrease for higher concentration of butanol. Collectively, higher percentage of alcohol produce cooling effect in the cylinder owing to high latent heat of evaporation, which reduces the temperature of cylinder, thus causing reduction in NO_x. Low cetane number of alcohol increases the ignition delay that results in more fuel supply to engine, thus leads to increase in BSFC. Very few studies have been reported on the wear of the engine with alcohol fuel blends; the abnormal wear was not reported for 10% and 15% dry ethanol [45]. Ethanol produces tribological problem with the possibility of contamination of the engine oil that likely to happen during cold start [46]. Alcohol removes additives from the engine oil and leaves the remaining raffinate to be more prone to oxidation [47]. The less wearing of the face and side of piston rings in a glow plug assisted neat methanol fueled engine was observed as compared to diesel fueled engine. Highest piston ring face wear was observed for methanol-diesel mix as compared to pure diesel or neat methanol, when operated in severe wear condition. The alcohol fuels lacks in material compatibility owing to acidic influence which it can have on automotive components. The causes of deterioration problems in the presence of alcohols in fuels are mainly its water content owing to hygroscopic nature and partly the existence of organic acids. Also, alcohols are polar diluents and henceforth, acidic to metal engine components [48]. Diesel engines have several components which make tribo-pairs. To elude the contact between the mating surfaces, lubricant is provided. The basic purpose of providing the lubrication is to diminish the friction, to reduce component wear, to provide shutting between piston and cylinder liner, engine cooling and to maintain the cleanliness. If these purposes are not fulfilled by the lubricant, it is said to letdown of engine oil and consequently, letdown of the engine. Engine oil degrades and becomes worse because of contaminations imported from the numerous causes. Different types of contamination affect the engine oil property. The types of contamination are fuel exhaust gases, dust acid formation, metallic particles,

water, soot, metal oxides and sand. Addison et al [49] have found the three probable cause of contamination of engine oil namely, solid, liquid and gas contaminations. The solid contaminations include wear debris; it harms the different mechanical parts of the engine and also increases the degradation of engine oil. Liquid contaminations include fuel and water which degrade the engine oil and additives do not perform well during operation. Gaseous contaminations include different combustion by-products which are responsible for corrosion on the surface of mechanical components. The contamination enters in the engine oil from several routes, such as, external ingression, internal ingression and built-in from manufacture and assembly. The hard particles induce from external sources which are mixed straight in the diesel fuel and suspend within the cylinder causing the wear of internal mechanical parts. Dust particles also enters to sump at the time of servicing and impart the detrimental consequences on the constituents of engine oil [49].

2.2 Present biofuels status in the world

The world reserves of petroleum are limited. According to an estimated data, the reserves of coal, oil, and natural gas will be ended approximately within next 218 years, 41 years, and 63 years respectively [50]. Crude oil reserves are endangered at the rate of 4 billion tons per year. With this rate, oil withdrawals will be shattered by 2052 [51]. It was reported that the liquid fuel utilization across the world will be increased due to transportation sector during year 2010-2040 [52]. Biofuels are being used in the engine to resolve the energy crises globally. Most of the country in the world started production of the biofuels since biofuels have enormous benefits over the petroleum fuels. The production of biofuels has exponentially increased from last two decades. Several countries have set their biofuel production targets such as, Renewable Fuel Standard (RSF) of the United States has targeted the 7.5×10^9 gallons of renewable fuel to be blended with the transportation fuels by 2012, and 36×10^9 gallons by 2022, which is approximately 20% of projected 2022 U.S. gasoline and diesel consumption. Similarly, The European Union (EU) Renewable Energy Directive (RED) has mandated a 10% renewable energy component in the transportation sectors of every EU member state by 2020 with 7% from

biofuels and 3% from vehicle electrification [1]. Average energy consumption in the transportation sector is advanced by 1.1% per year because of vehicles and industrial applications worldwide. According to critical review of the world energy reserves of oil, gas and coal as shown in the figure 2.1, there is a huge requirement of the fuel to be used in place of diesel. Biofuels are having the potential of to replace the diesel fuel. Rudolf Diesel, the inventor of compression ignition engine had started using peanut oil as a fuel in the compression ignition engine at its early stages. Vegetable oils, whether edible or no edible can be used as a biofuel in the engine, several researchers have tested the variety of vegetable oils as fuel and found that it has potential to be used as a fuel. However, they have experienced the number of problem such as, injectors choking etc. which leads to poor fuel atomization, poor combustion, lubricating oil thickening [3], injector-coking, injector deposits, crank-case oil polymerization, ring-sticking and injector pump failure [53]. There are several countries which is using the biofuel in their diesel engine operation. Oxygenated fuel have a tendency to blister cleanser, to reduce carbon monoxide, tail pipe emissions from hydrocarbons, and also, sulfur dioxide and particulate emissions. Unfortunately, regulated pollutant such as NOx emissions increased by utilizing oxygenated fuels [54].

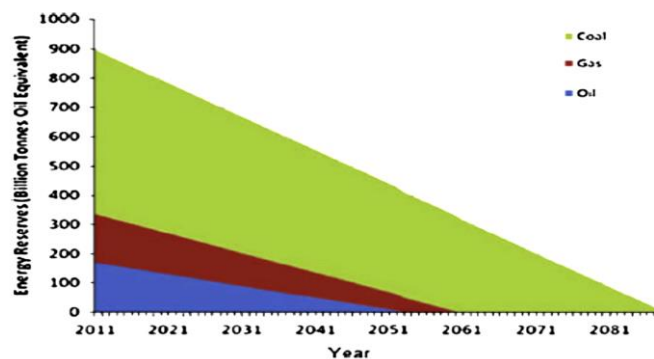
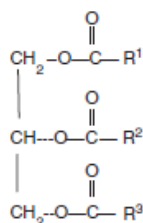


Figure 2-1: World energy reserves of oil, Gas and coal [51]

2.3 Biodiesel production

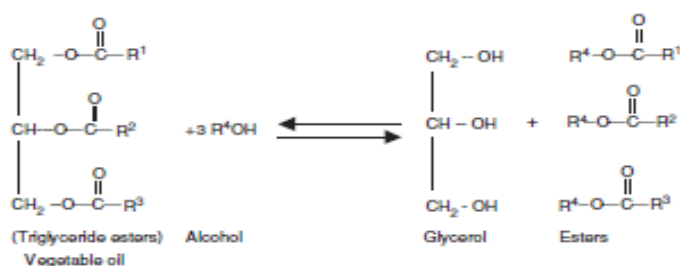
Many countries are producing biodiesel and using it in the diesel engine either blended with diesel or pure. Road transportation and agriculture are the main areas where the diesel engines are used as the energy supplier. The feedstock

for biodiesel production depends upon the climatic conditions of the country. In India, the major feed stock for the biodiesel is Jatropha, karanja, soya bean, and sunflower oil. However, other countries, like Japan, the main feed stock is waste cooking oil where as in Malaysia, palm oil is utilized for production of biodiesel. In Philippines, Jatropha and Coconut is mainly used for biodiesel production while in Thailand, Coconut, Palm and Jatropha are utilized for production of butanol [52]. The vegetable oils are used to produce the biodiesel as a feedstock. These oils are the blend of carbon-based composites, may be a straight chain compound or complex structure of proteins and fat. Vegetable oils are generally a set of triglycerides usually with a number of diverged chains of dissimilar lengths, and may have structure like shown below



where R^1, R^2 and R^3 represent hydrocarbon chain of fatty acids [50].

Biodiesel is formed using transesterification of vegetable oils. Transesterification is the process of bartering the alkoxy group of an ester compound by another alcohol. The reactions occur in the presence of catalysis. Catalysis may be a base or acid. In the transesterification process the triglyceride reacts with bio-alcohol and converts it to esters and glycerol. The reaction of formation of biodiesel may be shown by the equation.



where $\text{R}^1, \text{R}^2, \text{R}^3$, and R^4 are various alkali groups [50]

2.4 Butanol production

Alcohols are defined by the occurrence of a hydroxyl group (-OH) involved to one of the carbon atoms. The ethanol and butanol produced by the fermentation of the feedstock, which includes the sugar crops, starch crops and lingo-cellulosic crop and wood residues [54]. Bio-butanol production by fermentation of feedstock deals assured gains as compared to bio-ethanol; higher energy content, lesser water adsorption and acidic possessions, better combining capacities and the capability to be used in conventional compression ignition engines with no amendment in existed engine [55]. Butanol is produced by chemical synthesis from propene or acetaldehyde; the foremost promising to the present is microbiological synthesis that permits one to supply alcohol from renewable source in place of hydrocarbon feedstock [56]. Butanol was initially generated in United States in big volume from fermentation during World War I and II. N-Butanol is formed from fermentation by the Acetone-Butanol-Ethanol (ABE) process [54]. Ethanol has 36% oxygen, while the butanol has 22% oxygen [54]. At present, there are some industries in the People's Republic of China where bio-butanol is being produced successfully. There are 16 plants in the country producing the bio-butanol. The annual bio-butanol production of 150000 tons is estimated from the largest plant (JiAn Biochemical Co. Ltd). Yield of 100000 tons/ annum is estimated production of the bio-butanol by using the bacterial fermentation process, second largest plant in Guangxi. The feedstock of bio-butanol production in China are Corn and cassava starch. In Brazil, an industry is utilizing juice of sugar cane as a fermentation stock to produce 10000 tons of butanol per year. The other industries also commissioned in the different countries to produce butanol such as BP and DuPont. The other industries Butal Co in Switzerland, Arbor Fuel Inc. in United States, Tetra Vitae Bio Science in United States and Metabolic Explorer in France have developed an effective practice of bio-butanol production from lignocelluloses. An expertise of producing butyl alcohol by using fermentation of wood hydrolyzate by immobilized *C. aceto-butyllicum* cells is developed in Finland. In Russia (Tulunskii hydrolysis factory), wood hydrolyzate is used to produce bio-butanol on a large scale [56]. Nevertheless, ethanol has also been blended with

the diesel and considered a good fuel for diesel engine [57]. Butanol is considered as an alternative fuel due to its low vapor pressure, high octane number, good miscibility with gasoline and ethanol and high energy density; without changing the existing engines, fuel supply and distribution systems [56]. Using biofuels (n-butanol and biodiesel) at low-temperature combustion it is assumed that biofuel can reduce the soot and NO_x formation in the engine exhaust. The Energy Independence and Security Act (EISA) 2007 has mandated that the 36 billion gallons of biofuel is to be blended into US transportation fuels by 2022 [58].

2.5 Role of biofuels on degradation of engine oil

2.5.1 Wear of engine due to biofuels

Wear can be defined as the continuous material removal from the operating surfaces in the relative motion. There are different types of wear, such as, abrasive wear, adhesive wear, fretting wear, corrosive wear, erosive wear, and fatigue wear. There are number of tribo- pairs present in the engine such as piston ring and cylinder, bearings, valves, and crankpin. Whenever the engine operates these tribo-pairs generate the wear particles. These wear particles are exported by the lubricant (engine oil) into the crankcase thus, causing engine oil degradation and more wear among tribo-pairs in further operation. The biofuels play major role in the degradation of the engine oil. However the wear of the engine depends on the fuel used. Table 2.3 enlist the work performed using biodiesel and the effect on engine oil. Biofuels are able to lower the degradation of the engine oil in terms of metal contamination. However, some researchers reported that the viscosity and total acid number increases with time while the total base number of engine oil decreases. Use of biodiesel in the diesel engine in place of diesel fuel can decrease the wear of aluminum, chromium, iron and lead. Wear particles come in the sump by movement of piston and the cleaning by engine oil hold suspended [59]. Diesel lubricity comes naturally from occurring of polar compounds, which form a protective layer on the metal surface. Heterocyclic aromatics and nitrogen/oxygen compounds (rather than sulfur) were identified most important for lubricity. The mechanisms for lubrication vary with test methods

and operating conditions. For instance, monolayers of the additive, usually carboxylic acids or methyl esters, form on the surface; thus preventing contact between the two metal surfaces and reduces the wear [12]. The quantities of aluminum, copper, lead, and chromium decrease in the engine oil by utilizing safflower biodiesel. Nevertheless, wear concentration still persists within tolerable boundary values. The tested fuel blends are B2, B20 and B100. The highest value of iron in particular obtained through the use of B100 fuel. Thus, it was observed that all the blended fuels adulterated more than diesel fuel [60]. Wear of 50% jatropha blended fueled engine cylinder is comparatively lesser than mineral diesel fueled. The ash residue for 20% biodiesel fueled engine was noticed lower than diesel fuel. The metal rests like iron (Fe), copper (Cu), zinc (Zn), magnesium (Mg), chromium (Cr), lead (Pb) and cobalt (Co), were found less for 20% biodiesel fuel [61]. The pump plunger surface roughness was increased for B100 fueled engine. Carbon formation in the combustion chamber was found comparable for both fuel D2 (diesel) and B100 (biodiesel) [62]. The hygroscopic nature of karanja biodiesel may increase the wear and friction in the engine by producing corrosion in the engine components [63]. The finding of studies may be recapped with decrease wear of engine components, increase the viscosity of engine oil, sludge formation. However, some researcher [64, 65] found the higher iron metal, decrease in TBN of engine oil with time, additive depletion and sludge formation [66]. S. Arumugam et al [67] conducted 150 hour endurance test on diesel engine fueled with biodiesel. They used two engines of same capacity in same working condition of 80% load and both fueled with rapeseed oil biodiesel (B20). First Engine was supplied 20W40 engine oil and the other was supplied bio-lubricant (rapeseed oil based bio-lubricant). The engine oil samples were collected in every 25 hours of run. They found that iron and copper wear of engine with 20W40 engine oil (90ppm and 266 ppm) is higher than that of the bio-lubricant (73ppm and 15ppm), the reason for less iron wear being the less soot formation thus, less abrasive wear while the less copper wear was due to lower bushing and connecting rod bearing wear. The other reason was blow by gases mixed with lubricant of the sump. They also reported the reduction in soot with bio-lubricant due to the better combustion

efficiency and less blow-by. The probable sources of wear particle are shown in the Table 2.2.

Table 2-2: Sources of wear metal

| Metal | Source |
|---|------------------------------------|
| Iron (Fe) | Cylinder liner, valve, piston ring |
| Chromium (Cr) | Piston rings |
| Copper (Cu) | Bearings |
| Aluminum (Al) | Piston |
| Nickle (Ni) | Piston ring |
| Silicon (Si), Calcium (Ca), Phosphorous (P) Sulfur (S) | Additives |

The fuel dilution was found higher in the biodiesel fueled engine. Also the viscosity of the bio-lubricant is reduced more than that of the 20W40 with respect to their original viscosities. The reason is that the kinematic viscosity of engine oil diminishes at the start of the engine owing to shearing of the viscosity index improver that grows further in future owing to oxidation of engine oil and the fuel dilution.

Table 2-3: Comparison of engine oil contamination and wear due to biofuels and diesel.

| Researcher(s) | Engine type | Methods | Finding |
|--------------------------|---|---|--|
| A. Chausalkar et al [68] | 6- cylinder, 4 – stroke, 97kW, Diesel engine | Fueled with B5, 1000hr Engine oil (15W40) sample drawn every 50hr. and analyzed | No significant change in engine oil property, engine power. Normal wear. Viscosity higher. |
| A.K. Pandey et al [69] | 6-cylinder, 4- stroke 118kW, turbocharged CIDI diesel engine. AAS | Fueled with Karanja biodiesel, 100hr run, oil sample collected after each 20hr. | 35% lower wear debris in biodiesel than diesel. Viscosity increased. Less wear. |
| M.J. Thornton [64] | 4-cylinder inline 113kW, 3000rpm, 2.15 | Aging test, 750 hr., lube oil CJ-4. Fueled with 20% soya | Biodiesel |

| | | | |
|----------------------------|---|--|--|
| | liter HSDI diesel engine. | derived biodiesel blended with diesel. NAC system SCR system | dilution ranges 5-10% NAC system, Viscosity of lube oil decreased Iron wear increased 55ppm. Biodiesel dilution range 4-8%. SCR system. No change in viscosity. Iron wear increased 12ppm. TBN decreased 4.54mgKOH/g of oil. |
| M. A. Kalam et al [70] | 4 -cylinder, 4-stroke 1817cc, IDI Isuzu diesel engine 39kW, 5000rpm. Multi element oil analyzer for engine oil test | Engine run for three test fuel, diesel, at different speed. B7.5% (50ppm additive+7.5% palm oil methyl ester+92.5% diesel) and B15% (50ppm additive+ 15% Palm oil methyl ester+85% diesel) , 100hr for each fuel, engine oil (SAE-40) sample taken after every 10hr. | Fe (26ppm) in B7.5% 29ppm in B15% 36ppm in diesel. , Cu, Al, Pb wear particles reduced with POD (Zn, Ca) additives component depletion decreased with POD. Viscosity of engine oil reduced with POD. TBN reduced with POD |
| Dilip Kumar Bora et al[71] | Kirlosker, 5.9 kW, 4 stroke, single cylinder diesel engine, water cooled AAS | Run for 512hr, at different loads, fueled with karanja biodiesel 20% blend. Engine oil (15W-40) analyzed. Sample collected after 150hr. each. | Fe wear reduced with the use of biodiesel. Viscosity at 100°C. Lowers with oil usage time, but less compared to diesel fuel. |
| Anderson Favero Porte [65] | Single-cylinder tramontini (TR) 22 | Engine run for 280 hr. fueled with residual frying oil biodiesel. | Kinematic viscosity decreased. |

| | | | |
|----------------------------|---|---|---|
| | Engine with 22 CV power at 1,800 RPM, | Engine oil sample collected after every 50 hr. of usage | Wear metal (Fe, Al, Cu, Cr Pb, and Mn) contamination increased with time. TAN increased. |
| Shailendra Sinha et al[72] | 4 cylinder, 4-stroke, M&M Ltd., India/MDI 3000, 55hp, 3000rpm | Engine runs 100hr, fueled with rice bran methyl ester 20% blended with diesel | Wear particles (Fe, Al, Cr, Cu, Ni, Zn, and Pb) higher initially, after 20 hr. reduced with biodiesel. |
| A.K. Agarwal et al [73] | Single cylinder, 4- stroke, 4kW, 1500rpm Diesel engine | Engine runs 512hr. Fueled with 20% linseed oil methyl ester AAS oil analysis | Wear particle (Al, Fe, Co, Cr, and Mg) approximately reduced 35% than diesel. |
| Levent Yüksek et al[74] | Hatz Diesel Co. Germany Model E673 LHK Type single cylinder, 4-stroke, air-cooled Diesel engine, 4kW, 3300rpm | Engine fueled with 100% RME run for 150hr, 85% of full load, Oil (SAE10W-40) sample collected after every 25hr. | Fuel dilution 3.5% increased, Wear of (Fe, Cu, Al,Cr,Sn) increased. TBN decreased, TAN increased Viscosity. |

Schumacher et al [75] analyzed a compression ignition engine using engine oil analysis. The engine was fueled with 1%, 2%, and 100% biodiesel and they reported that the wear of engine components was found to be at normal rate. Agarwal et al. [53] assessed the diesel engine with the help of engine oil analysis by atomic absorption spectroscopy. The engine oil sample was collected after 512 hour run of the engine. They found that the wear metal in diesel fueled sample was higher than the biodiesel- fueled sample. The wear of different engine components abridged up to 30% due to surplus lubricity delivered by the biodiesel. Ozcelik et al. [60] evaluated the diesel engine by engine oil analysis. They noticed that the quantities of Pb, Al, Cr, and Cu in

the engine oil get reduced by using safflower biodiesel and blends in comparison of diesel. They also observed the improvement in lubricity and formation of oil film between mating surfaces by utilizing biodiesel. Sinha and Agarwal [76] inspected the medium-duty diesel engine with the help engine oil analysis after a 512- hour endurance test. The engine was supplied with a blend of rice bran methyl ester of 20% and 80% diesel and appraised the result of biofuel on engine internal component wear. They assessed that the wear metal present in the engine oil from blended fueled engine was higher than the (B20) fueled engine oil sample. Agarwal et al. [77] carried out an endurance test of 512-hour on diesel engine to assess the engine wear. The engine was fueled by biodiesel made up of linseed oil methyl ester in the proportion of 80% and 20%. They found higher wear for diesel fueled engine than the blended fuel engine. Wear concentration of different metals like chromium (Cr), copper (Cu) and iron(Fe) are found to be lower in the engine oil of the mixed fueled engine as compared to the engine oil from the diesel-fueled engine. Abhishek Sharma and S. Murugan [78] conducted endurance test of 100 hours as per IS: 10000 codes. The engine was supplied with the blends of tyre pyrolysis oil and jatropha methyl ester (JMETPO20) as fuel. They change the engine oil after every 25 hours of run for its analysis. The outcomes disclosed that the kinematic viscosity of the JMETPO20 fueled engine oil gets reduced more than the diesel fueled engine, the reason being moisture content. Due to the moisture content additive are dropped out and fuel dilution is increased. Moreover, they observed that the wear (iron and copper) of the engine is higher for the JMETPO20 fueled engine than the diesel fueled, reason being the more fuel dilution in the engine results partially dissolved lubricant that increases the coefficient of friction. Pandey and Nandgaonkar [69] carried out an endurance test of 100 hours on a turbocharged, direct-injection diesel engine fueled with karanja oil biodiesel. The engine oil was analyzed in atomic absorption spectroscopy. They observed that the karanja biodiesel-operated engine shows 35% less wear metal such as aluminum nickel, chromium, copper, lead, and iron than the diesel fuel operated engine. Bora et al. [71] assessed the diesel engine wear after a 512-hour durability test by using engine oil analysis and stated that the B20 fuel did not produce any

significant harm to the engine despite of changing the engine oil properties. The contact of cylinder liner and piston ring of the engine is considered as the boundary lubrication phenomena. Very thin layer of lubricant involves in protecting the contact between the mating surface of piston ring and liner. The engine oil provides the lubrication and also the sealing. The engine oil degrades due to metal contamination. Worn out metal particles suspend in the oil sump produce three body abrasion. Three-body abrasion is a phenomenon of abrasive wear when foreign particle trap between to mating surfaces, the particle rubs the both materials while sliding. Further, wear of engine component increases with load, thermal condition, speed, surface hardness, etc. Wear metal particle is most responsible matter which contaminates the engine oil severely. The conjoint sliding contact parts of the any engine are cam, bearings, tappet, piston ring, crankshaft piston and cylinder liner etc. [79, 80]. The wear rate of engine increases rapidly with the metal contamination of engine oil. The combustion gases leak out from the cylinder due to non-uniform wear of cylinder. Hence, the efficiency of the engine reduces [80]. The friction and wear depends upon the sliding or rolling contact of the surfaces. The computable assessment of metal existent in the engine oil indicates the wear of the engine internal parts. Filter plugging, injector coking, and increasing moving part sticking, are the conjoint difficulty for utilization of biodiesel. Biodiesel of unsaturated molecules and compositional effect enhances the corrosion and oxidation [79]. The engine oil constituents change with time and usage. The changes are explained normally with relationship between time and additive depletion of engine oil.

2.5.2 Fuel dilution of engine oil due to biofuels

Passageway of engine oil contamination of crankcase shown in the figure 2.2. The engine cylinder is associated to little volumes typically named crevice due to their very fine entrance. The burnt gas enters and exits from the crevices with the change of cylinder pressure during the operation. The largest crevices are the volume between the cylinder wall, piston rings, and piston.

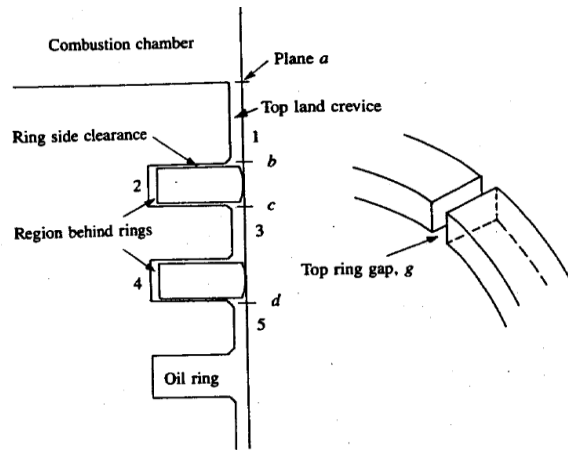


Figure 2-2: Region of blow by of piston ring [81]

The other crevices volumes are slit around the fuel injectors, gaps around the cylinder head, intake and exhaust valve. In the compression stroke of the cylinder the pressure increases and the mixture of unburned charge is expelled to the crevice region [81]. The unburned fuel mixture is scrapped by the piston ring with the lubricating oil. The thermal expansion of the piston rings is very less hence the slit among the cylinder wall and piston rings is broader due to the low wall temperature. At the low temperature of the cylinder wall, the viscosity of engine oil is higher that makes thick film and whenever this film is thick, the oil fails to seal the piston and cylinder contact region. During the engine operation in cold working condition, the unburnt fuel gets condensed and wiped by the piston ring which finally mixes with lubricating oil. Biodiesel may contain some glycerides which is extra hotness delicate than the lubricating oil. Because of temperature cooking effect on the heated engine components, the result could be stuck piston ring and improper sealing, which may increase the fuel dilution [2]. Siti Norbaria et al [82] reported that when the biofuel RBDPO (Refined Bleached and Deodorized Palm Oil) is mixed with the engine oil in different percentages of 10, 20, 30, 40, 50 and 100, the boundary condition of dilution in the engine oil is achieved at 20%. In the diesel engines, fuel dilution is occurred by the excessive idling and defective injectors. The existence of excessive fuel in the lubricating oil lessens the strength of the oil film. The reason behind this is the reduction in viscosity leading to increase in metal-to metal contact, friction and wear [82].

2.5.3 Oxidation of engine oil due to biofuels

In the instance of oil oxidation, the reaction outcomes is the consecutive accumulation of oxygen to the base oil molecules, to produce an amount of diverse compounds comprising aldehydes, ketones, hydro peroxides and carboxylic acids [2] . The hydrogen sulfide emissions of combustion exhaust gas reacts with water and generate sulfuric acid. Sulfuric acid is having corrosive nature and may corrode the bearings and copper oil coolers of the engine. The lubricant provides base to control the acid formation from hydrogen sulfide as well as weak acid formed from the oxidation of the oil. However, the metallic detergent additives of base can increase the sulfated ash (SASH) content in the oil [83]. Engine oil moves in the cylinder bore lengthways with the action of the piston rings. The circumstances in the cylinder are very severe, meanwhile the fuel obviously blow up numerous times a second, generating very high pressures and warmth causing fuel to generate harsh substances when incomplete combustion occurred. The heat generated by combustion is sufficient for moderate oxidation of the engine oil that leads to production of organic acids (i.e., oxidized hydrocarbons) except the oil's antioxidant blocks the oxidation and acid formation [84]. Alcohols have less Sulphur content and additional oxygen than the fossil-based fuels. On the opposite facet, alcohol fuels, normally generate advanced phase emissions owing to higher vapour pressures whereas their low energy density causes a negative effect upon engine performance. However, the appallingly low cetane number limits the usage of immaculate alcohols in diesel engines; they ought to be blending with diesel without modifications within the engine equipment [85].

2.5.4 Nitration of engine oil due to biofuels

The higher combustion temperatures in the engine cylinder form nitrogen oxides (NO_x). NO_x triggers the oil nitration. Due to that oxidation of oil increases and form the insoluble and acids leading to increase viscosity, reduced Oil Drain Interval, deposit formation in the piston, and corrosive wear [83]. Nitration of the oil may lead to early thickening of the engine oil. The nitration occurs due to the improper exhaust of the combustion gases and

byproducts, incorrect air-fuel ratio, lower operating temperature, and leakage in piston seals.

2.5.5 Soot loading of engine oil due to biofuels

The unsaturated hydrocarbon, incomplete combustion and acetylene hydrocarbon produces soot in any engine. Basically, soot is a carbonaceous particle. The tail pipe emissions and fuel consumption are highly affected by the harmful effect of the soot contamination of engine oil [86]. Soot reacts with the additive content of the engine oil that may result an increase in the wear of the engine and reduction in the efficiency of anti -wear additive. The surface of the engine component and the soot particle come into the contact because of the disruption of the oil film. Soot element possess diameter of 0.01micrometer to 0.8 micrometer and acts as the abrasive material and reduces the ability of the engine oil to form anti-wear film on the engine components' surfaces. Therefore, the soot abrasion and surface to surface contact starts. The higher molecules accumulation starts with the degradation of the engine oil [87]. The utilization of biodiesel in the engine as fuel improves the combustion that increases the occupant period of soot particles inside the combustion chamber of the engine. It allows more oxygen to oxidize the soot and hence there is a reduction of soot [88]. The study of presence of soot particles in the engine oil in the engine fueled with biodiesel shows that the utilization of biodiesel in the diesel engine decreases the soot loading of engine oil, thus, less wear of engine components [89]. Due to low combustion temperature, lower boiling point and higher distillation temperature [90] the engine internal temperature reduces because of the slow burning of rapeseed oil. Hence, there is a reduction of the soot particle. The soot production in the engine is highly appreciated by the cylinder temperature and air-fuel ratio. The combustion of fuel with insufficient oxygen forms soot. Using biodiesel as a fuel in the engine results in less production of deposit and carbon during the ignition thereby less residue adulteration of engine oil. The soot level in the engine oil is considerably less with B20 fueled engine [79]. Soot development reduces through the utilization of biodiesel as a fuel for diesel engine because the biodiesel contains more oxygen which arouses the

oxidation of soot rapidly [91]. The study of soot loading in engine oil is shown on Table 2.4. One can observed from the findings of the research on soot loading that biofuel utilization in the engine produces less soot than diesel fuel and it easily gets oxidized. Haifeng Liu et al [5] found that the n-butanol suppresses the soot generation more effectively than that of biodiesel indicating higher soot reduction ability of butanol.

Table 2-4: Soot contamination of engine oil due to biofuels

| Researcher(s) | Equipment | Method | Finding |
|--------------------------------|------------------------------------|--|--|
| Anthi Liati et al[92] | 4- Cylinder in line Diesel engine. | Soot loading for 27h with different blend engine fueled with biodiesel (RME) and their blend, Diesel particulate filter analyzed for soot, OM, SEM | B100- DPF, less soot than the diesel DPF. Biofuel derived soot easily oxidized compared to diesel soot. Soot cake thickness of Diesel fuel was 200-250 micron while B100, negligible soot. |
| P. Barry Hertz et al [93] | IDI Isuzu 1.8 L, Diesel engine, | Fueled with canola biodiesel Highway driving, cold weather, 3600km | Lower suspended carbon soot in the engine oil in canola fueled engine 2.0% as compared 9% in diesel fueled. |
| Shrawan Kumar Singh et al [94] | Two Cylinder Diesel engine | Fueled with EGR of 25%, 96 hr. | Soot increased with EGR, increased wear. |
| Shailendra Sinha et al[72] | Four stroke DI engine 2520cc | Fueled with 20% rise bran oil methyl ester, run at different load | A lower soot formation with biodiesel fueled engine. |
| Bong Ha Song et al [95] | 2700 cc 5- Cylinder Diesel engine | Run 500hr, fueled with diesel | Soot oxidize with post injection, increase exhaust gas temperature 700-800 ⁰ C |
| R.Ramprabhu et al [96] | 4-stroke, DI diesel engine, 63 BHP | Engine run for 1000hr, fueled with D100, B10-J and 50000km run | Soot decreased 50% in the case of biodiesel fueled engine than that of |

| | | | |
|---------------------------|--|---|--|
| | | engine fueled with D100, B20-K | petro diesel. |
| S. K. Mazumdar et al [97] | 6- cylinder in-line turbocharged, 280hp/ | Endurance test run for 2250 hr. Fueled with diesel. /TGA method for soot | Soot loading increases with time, but very less |
| Aaron Williams et al[98] | 6- cylinder, Cumming ISB engine with EGR, 224 kW diesel engine DPF | Engine run for 350 minute, 2000 rpm, 27.1 N-m fueled with B20, B100 and diesel | B100 soot contains 20-25% oxygen than diesel soot. Soot from B20, B100 reactive in oxygen. |
| A. Chausalkar [68] | 6- cylinder, 4 – stroke, 97kW , Diesel engine | Fueled with B5, 1000hr Oil sample drawn every 50hr. Engine oil (15W40) analyzed | Soot less than the diesel |

Anthi Liati et al, have examined the 4- Cylinder in line Diesel engine equipped with diesel particulate filter and fueled with biodiesel (RME) and their blends. The engine is allowed for soot loading for 27h with different blends. After the analysis of the diesel particulate filter, they found that the soot formation in the B100 fuel is less than that of diesel fuel. Biofuel derived soot gets easily oxidized as compared to diesel soot. Soot cake thickness of Diesel fuel was 200-250 micron while B100 (RME) soot was found to be of negligible thickness. Similar study was carried out by P. Barry Hertz et al, with the IDI Isuzu 1.8 L diesel engine. The engine was fueled with canola biodiesel and is driven on the Highway in the cold weather season for 3600 km. They found that the Lower suspended carbon soot in the engine oil in canola fueled engine was 2.0% as compared to 9% in diesel fueled. Shrawan Kumar Singh et al [99] examined the two cylinder diesel engine operated for the 96 hour with exhaust gas recirculation (EGR) of 25%. The results show that the soot increases with percentage EGR due to low cylinder temperature responsible for increased wear. Another study by Shailendra Sinha et al [76] on the four stroke DI 2520 cc diesel engine fueled with pure diesel and blend of diesel and 20% rise bran oil methyl ester. The engine was operated at different load

condition and they found that soot is lower for biodiesel (rise bran methyl ester) as compared to that for pure diesel. A similar study was carried out by Bong Ha Song et al, on a 5 cylinder, 2700 cc, diesel engine fueled with diesel and operated for 500 hours. They found that Soot oxidizes with post injection and exhaust gas temperature increases to 700-800⁰C. R. Ramprabhu et al [11] examined a 4-stroke, 63 BHP DI diesel engine fueled with D100 and blended fuels (B10-J) and (B20-K) for 1000 hr and 50000 km run respectively. They found that Soot decreases by 50% in the case of biodiesel as compared to that of petro diesel. Soot is firstly forms due to the presence of carbon in diesel fuel; the other species attracted towards the soot due to its molecular structure and create the bigger soot. This may reinforce the viscosity of the fluid layer thus, it becomes thicker [100]. Soot intermingles in the engine oil and rise the wear of engine components. The viscosity of the engine oil decreases due to soot contamination [101]. Stodola J. et al [102] have proposed the engine oil degradation with three stages scavenging followed by operation and equilibrium. The 25% of the physical property of engine oil reduces in the scavenging running of the engine for less time. In second stage whenever the engine completes the thousands kms of operation, the property changes nearly by 50%. Finally, the equilibrium stage proceeds when regeneration processes eradicate the growth of degradation of engine oil. The abrasive wear is the result of carbon residue in the lubricant and late combustion [103]. Due to inadequate lubrication in the cylinder, carbon particle remains un- scavenged, which lead to carbon deposit. Wear depends upon the different parameter like, load, speed, environmental condition, temperature, soot formation, and intruder material. Finally, the wear debris mixes with lubricants and produces the abrasive wear. Most of the researches reported that the soot generation lowers with the biofuels as compared to diesel; it means engine oil degradation may be reduced using biofuels in the diesel engine and can serve for extended life of engine oil with respect to soot formation [72, 96]. However, the particulate material and exhaust gas products in the recirculated gas contaminate the engine oil by adding soot content. Soot increases by application of EGR. EGR reduces the cylinder temperature and increases the particulate matter [87, 104].

2.5.6 Water or moisture ingress in engine oil due to biofuels

Hanbey hazar et al [105] examined a 4 stroke Lombardino 6 LD 400 mono cylinder compression ignition engine. The engine was supplied with blend (10\%methanol +90\% diesel) fuel and operated for 100 hours at no load. They detailed that the heaviness of engine oil from the methanol mixed powered engine is higher than that of the diesel energized engine. Methanol diminishes the engine oil property and rise the admission rate of particulate matter within the engine oil. Due to hot temperature produced by methanol, the fractional chemical reaction happens and causes jam of piston ring within the slot. It supports the growth in wear and lowers the viscosity of engine oil of methanol mingling fuel engine below that of the diesel burning engine. Thus, methanol deteriorates the engine oil and augments engine wear. Blow- by of the engine may increase the fuel and condensed methanol up to 20% in crankcase [47]. The quantity of water in the configuration of alcohol originates acidic influence on the fuel assembly of the engine [105]. The emulsification of engine oil increases the thickness and viscosity of engine oil [106]. Water can instigate from various causes and produce water contamination of the oil. Even the low quantity of the water in lubricating oil may pollute the engine oil and is very harmful to the engine. The water ingress in the lubricant by moisture or leakage in cooling water jackets [107]. Water in engine oil might be introduced in the two stages, scattered (water relaxed beneath the satiety point) and free water. Dispersed water makes no mischief to engine part however free water erodes the engine subdivision, ingests added substances (additives) within the engine oil and curtails the engine life.

Free water oxidized the base oil of the lubricant rapidly, rinses a few added substances (additives) that are pulled within the water [108]. The impact of water abuse might be understood within upper combustion chamber area where the elasto-hydrodynamic lubrication presents. Water and ionic mixes could influence and quicken the erosion of engine component material [109]. Water tainting happens in the engine oil in three structures; emulsion, dissolved and free water. The free water can be effectively expelled from the engine oil while emulsion is hard to evacuate. When water and metal exists in the engine oil, antioxidants agents expended quickly prompting erosion.

Slurry and varnish develop fractional positive and negative charges that prompt the fascination amongst water and polar added substances (additives) as well as solvency of water increments with the oxidized engine oil. Hydrolysis is the other response that destroys the properties of the engine oil [110]. The water pollution of engine oil may prompt rusting of ferrous segments and advances emulsion in the engine oil [111]. Humidity is harmful to mechanical framework. it inadequately affects the oil added substances (additives) causing rusting surfaces of mechanical components and weakening of elasto-hydrodynamic lubrication. Polar nature of the water atom underpins ionic portability and increment compound assault to the copper, lead and other responsive metal surfaces. Elasto-hydrodynamic lubrication relies upon one of a kind weight consistency property of mineral oil and manufactured (synthetic) engine oil. [112]. Water etching is like erosion that happens in bearing raceways as a consequence of engine oil dereliction because of water contamination [113]. Oil can assimilate water straight forwardly and ingested water dependably breaks up in the oil, and emulsify because of the pressure and temperature. Uncalled for rummaging and exhausted liner could clue the water defilement of engine oil. Free admission of water in engine oil is because of buildup of dampness (condensation) in the holder. In blends with oxygen, warmth and metal impetus water is known to advance oxidation and yields peroxides. Additionally, vast measure of water emulsion can diminish the heat conveying limit of engine oil by bringing down the viscosity [113].

CHAPTER 3: FUNDAMENTAL OF LUBRICATION AND LUBRICANT

3.1 Introduction

The fundamental of engine oil, its properties and functions are discussed in this chapter. The number of standard of engine oil is used as per given application and working environment. The prepared basic grades are SAE grades. This classification is done on two categories as single grade and multi grade for single grade the nomenclature is given as SAEXX and for multi grade SAE XXWXX. Every number shows a range of viscosity at °F. The W stands for winter. The capacity of engine oil is vital for the smooth running of engine. Engine oil has to play many roles in the engine. Lubrication is attained by evolving the Physico-chemical characteristics of the lubricant. Physical properties such as thermal conductivity, viscosity, density, temperature-pressure-viscosity relationships, and heat capacity decide the working capacity of the lubricant under the hydrodynamic lubrication [114]. Engine oil is used to diminish the friction between the mating surfaces, providing lubrication, reduce engine component wear, provide the sealing, facilitate cooling against thermal exposure, provide cleaning for better movement of engine internal components and provide neutralization against the corrosive effect of the acids. The main function is summarized in the Figure 3.1.

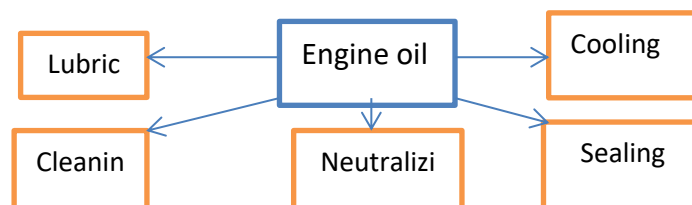


Figure 3-1: The main functions of the engine oil

3.2 Viscosity

Lubrication is the one of the prime functions of the engine oil. Viscosity is involved in the lubrication, which reduces the wear and friction between the two metal components during the operation of the engine. Viscosity is a measure of resistance offered by the fluid to one layer to adjacent layer. It is therefore, the engine oil of higher viscosity produce more resistance between the fluid layers hence the higher shear force and relative movement is required to get the hydrodynamic lubrication. However, higher viscosity provides higher load bearing capacity [2]. The variation of viscosity with the temperature is shown in figure 3.2. The Vogel's equation gives the temperature and viscosity relationship

$$\eta = \eta_{ref} e^{\frac{b}{T+\theta}} \quad (1)$$

Where ,

η is the dynamic viscosity, T is the temperature and b and Θ are constants.

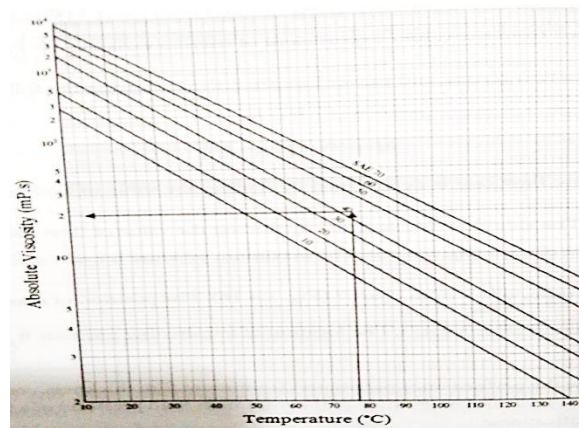


Figure 3-2: Variation of viscosity with temperature [115]

The low viscosity oil flows very easily due to its lower molecular composition hence, it requires less force to move and to generate the hydrodynamic lubrication. There are two types of the viscosity viz dynamic viscosity or absolute viscosity ($N\cdot s/m^2$) denoted by (μ) and kinematic viscosity (m^2/s) denoted by (ν). Referring the figure 3.3, Dynamic viscosity is the force required to glide the fluid between two smooth plates parallel to each other.

Shear stress (τ) is the ratio of the tangential force (N) to the unit area (m^2) of the moving plate at the constant velocity v (m/s). [2]. Let us consider the two plates are separated by fluid film h . The tangential force F is applied on upper plate of area A (m^2) to move the plate from velocity v_1 to v_2 . Consider v_1 initial velocity of plate and as v_2 final velocity of the plate. Change in velocity $dv = v_2 - v_1$ and is moving with velocity v (m/s). According to the Newton's law of viscosity the shear stress

$$\tau = \mu \frac{dv}{dx} \text{ N / m}^2 \quad (2)$$

But the

$$\text{Shear stress } \tau = \frac{F}{A} \quad (3)$$

$$F = \mu A \frac{dv}{dx} \quad (4)$$

Where μ be the dynamic viscosity.

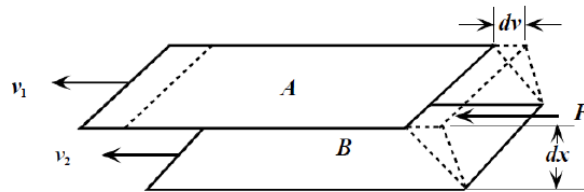


Figure 3-3: Dynamic viscosity and shearing of the liquid film [2].

The dynamic viscosity is the very significant which is related to the mechanical stress of the lubricant during the operation with respect to shear stress and shear rate. The ratio of the dynamic viscosity to density ρ (kg/m^3) of the fluid is known as kinematic viscosity (m^2/s).

$$\nu = \frac{\mu}{\rho} \quad (5)$$

Imperative to intensification of the viscosity of oil of sufficient load carrying capacity, viscosity modifiers (VM) or additives are mixed within the base oil. Viscosity modifiers are the polymer of the higher hydrocarbon. The volume of these polymers is increased with increase in temperature. The decrease in the viscosity of the base oil is compensated by the increase in the volume of the

viscosity modifier polymers [2]. The shearing of the oil takes place because of the relative motion of molecules of the oil between each other related to the engine moving components. Engine oil should have better load carrying capacity, wear reduction and quick hydrodynamic lubrication provider.

The main aim of applying lubrication is to decrease the friction between the two mating surfaces having relative motion. The friction is expressed by a dimensionless friction coefficient (f). The coefficient of the friction is defined as the ratio of friction force (F) to the normal force (F_n).

The entire engineering surface has roughness known as asperities. The asperities come in the contact and exposed to very high shear stress in the absence of lubricant. The lubrication of mating is based upon the two principles: the fluid pressure rise to keep separation between the surfaces and prevent contact; sacrificial surfaces as chemically active films to prevent the main surfaces from shear stresses due to rubbing and abrasive action between surfaces. Lubricating oil is used to create hydrodynamic pressures to provide the support against the applied load. When the load is high /or speed is low, the additives generate the protective film in boundary surfaces which, protect the asperities contact [114]. The Stribeck curve (figure 3.4) shows the three regimes of lubrication, namely, boundary, mixed and hydrodynamic lubrication. When load is high and viscosity of oil and the sliding speed is low, boundary lubrication is generated where the partial metal to metal contact is generated and coefficient of friction is increased. This happens through the engine action, for example, at the reversal point of the pistons or at the engine start [2]. In the hydrodynamic region, the lubricating oil makes the thick film of lubricant by which sliding surfaces are separated completely. Lubricant reaches to the loaded zone of the engine by the motion of the engine's internal components and produces the hydrodynamic lubrication. The pressure is generated in the lubricant and makes the wedge shape at the loaded zone. The pressure maintains the film thickness of lubricant and holds the engine parts separated from each other [120]. The friction is generated due to the shearing of lubricant. The hydrodynamic lubrication reaches toward the boundary lubrication when both the viscosity of the engine oil and sliding speed decrease and load increases. Due to this, the coefficient of friction is raised

sharply. In the mixed regime the load is taken by both the lubricant and surface of the solid [84].

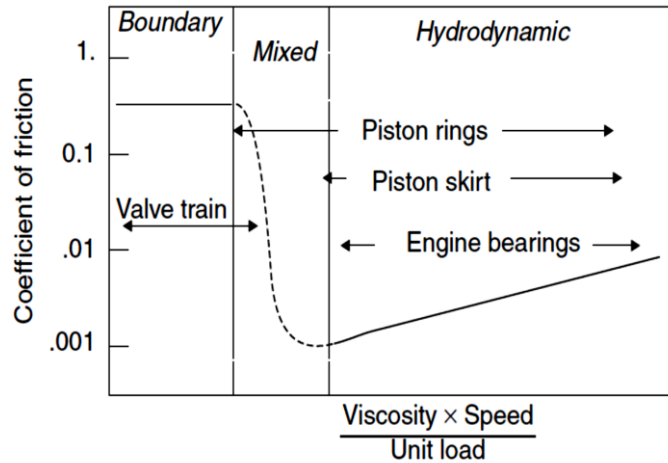


Figure 3-4 Stribeck diagram of the boundary, mixed and hydrodynamic lubrication the friction coefficient f is plotted in vertical axis and on the horizontal axis the Sommerfeld-Number [84].

Engine oil contains two additives namely detergent and the dispersant. They are responsible for the cleaning of the sliding surfaces. The additives contain non polar and polar molecules. Dispersant is a metal free and ash less additive which consists of long and non- polar olephite. The dispersant additives collect the contaminant either solid or liquid which ingress in the oil during engine operation and restricts the cold sludge and sedimentation formation by keeping the contamination in the suspension. Sludge may chock the oil gallery; filter rings and valves, piston grooves thus, leads to catastrophic engine failure or advance accelerated oil degradation. The other cleaning additive is detergent which is mixed in the engine oil. The molecule structure of the detergent contains higher strength of the polar head and shorter tail [2]. Usually, detergents are the alkaline-earth metallic salts of salicylates, sulfonates and phenates. The alkaline earth metals, typically calcium (Ca), or magnesium (Mg) can hence be regarded as the purposeful components to identify and specify type of the formulated detergents [121].

The main function of the detergent is to eliminate carbon deposits, lacquer, and varnish formation on the hot engine parts. Detergent plays important roll to prevent the ring sticking during the operation of engine working on high

temperature. The detergent market is covered by Calcium sulfates up to 65%. Detergent additives react with the by-product of oil degradation and combustion in numerous means, including neutralizing acidic components entering the lubrication oil, dispersing and suspending solid particles. The synthesis of detergents is done to control rust, inhibit oxidation as well as inhibit corrosion and limit deposit formation [122].

The other important role of lubricant is to neutralize the acids which form during the engine operation. Neutralization of the acids that form from the combustion gas, due to by-product of the oxidation of the engine oil and from the nitration process is performed by the engine oil additives. The acid produced by combustion gas, come in to direct touch with the engine oil. These acids generate corrosive wear of the engine components and it can also produce the deposits in the hotter part of the engine. So, the engine oil must have the alkalinity. To provide the alkalinity to the engine oil, the alkaline detergents (sulfonates and phosphonates of alkyl) additives are used and it is characterized by the Total Base Number (TBN) in mg of KOH/g of oil. During the engine operation for long time, the detergent degrades and lose the neutralization property which results in the increase in the acidity of the oil. Decrease in TBN and increase in acidity is an indicator of the oil drain. Total Acid Number (TAN) is a measure of the acidity of the engine oil [123]. Generally, it is advised to change the lube oil when TBN reduced up to one third of maximum TBN value. The detergent additives are used to provide the total base number to the engine oil to improve the cleaning properties. Detergents normally used have additional magnesium-carbonate or calcium-carbonate in the compound that is enclosed by the detergent particles in the form of micelles (an aggregate of molecules in a colloidal solution). The total base number offers a high alkaline level of the oil and thus anticipation of acid form up in the engine oil. However, it increases the ash formation due to burning of detergent during the engine operation [2]. Total base number is a measure of ability of lube oil to counter the acid attacks generated in the lube oil during the operation. Total base number is provided in the lube oil to resist the acid formation or to neutralize the acid and prevent the engine component

from the corrosive wear. Corrosive wear occurs due the oxidized engine oil at high temperature generated in the engine at the time of combustion.

The lubricants are designed using petroleum, or the mineral oil. The base oil should possess the enough viscosity to provide a lubricating film at the time of operation and also it should remove the heat from the mating surfaces to avoid the power loss. It must be stable against the thermal stress and oxidative stress, possesses low volatility and able to minimize friction and wear. Also, it should be able to melt chemical additives and chemically unreactive to the metal surfaces, rubber seals and gaskets for instance [114]. The total acid number is the amount of a base which requires titration a tester using a specific solvent to a certain end point by means of an appropriate recognition system. It is expressed in mg of KOH/g of oil [124]. The base oil of the lubricating oil is oxidized during operation and produces the weak acids. Weak acids are to be neutralized by the base of lubricating oil and if not, it becomes as TAN. Some acids may be generated by combustion blow-by which is not neutralized by detergent and remain in the lubricant and TAN increases [125]. TBN offers cooling against the heat generation in the engine due to thermal loading. The heat is removed from the lubricating point by applying the heat transfer phenomena of conduction and convection [2].

Anti-wear and friction modifier additives act on the surface. So it should be near to the surface or at the surface for smooth function. Therefore, the element of anti-wear additives is opted to be active on the surface in terms of polarity and molecular size. Zinc dialkyl-dithio-phosphate (ZDDP) is most common anti-wear additive which produces reactive and polar acid phosphate in the thermal decomposition. Blends of different ZDDPs with diverse decomposition temperatures offer safeguard to the different parts of an engine while being operated under the different levels of temperatures and the stresses such as the contact between the piston ring and cylinder liner at high temperature. Eventually, this contact zone needs a high-temperature ZDDP while the cam-lifter contact operates under low temperature [114]. The adding of ethanol produces a boundary film, which does not exist for the base oils. The film thickness at the lubricating points reduces with addition of ethanol.

Ethanol minimizes the friction at high speeds allied with a lessening in the viscosity of the lubricant. However, at low speeds, higher friction is generated due to lack of boundary layer. Film thickness and friction are not changed with the hydrated ethanol as compared with anhydrous ethanol [46]. The utilization of ethanol in diesel engines as a fuel carries some tribological problems due to the likelihood of contamination of the lubricant with ethanol [46].

3.3 Viscosity Index

Oil viscosity does not depend on the temperature only thus it is not a function of temperature only. The rate of viscosity change with the temperature may differ across oil having same grade. So, it is required to have one which can give relationship between temperature and viscosity. So, Viscosity Index (VI) is introduced which is considered to have two oil having same viscosity at 100⁰C but differs at 40⁰C. The VI of the engine oil is determined by the standard D2270. The petroleum industry recognized this and developed standardized curves of viscosity versus temperature. Measurements were standardized at a low rate of shear flow (typically a few hundred s⁻¹) and at set reference temperatures (40⁰C and 100⁰C). The viscosity index (VI) was introduced to describe the temperature dependence based on these two measurement points [116]. Viscosity index (VI) is an empirical number which indicates the variation of viscosity of oil with the temperature. If viscosity index of oil is high, then the change in viscosity of oil will be less with temperature. so, it helps in the cold starting problem of the engine. If U is the kinematic viscosity at 40⁰C of the oil whose VI is to be calculated, the viscosity index (VI) is given by

$$VI = 100 \left[\frac{L - U}{L - H} \right] \quad (6)$$

Where,

L = Kinematic viscosity at 40⁰C of an oil with VI=0 having the same kinematic viscosity at 100⁰C as the oil whose viscosity index is to be calculated, mm²/s.

H= Kinematic viscosity at 40⁰C of an oil with VI= 100 having the same kinematic viscosity at 100⁰C as the oil whose viscosity index is to be calculated mm²/s.

3.4 Density

Density is a main property in lubricants and also in all other fluids. It is the amount of the mass of a substance relative to a recognized volume. Lubricants generally have lesser density than water. The object with lower density than the water will float in water. The moisture contain in the lube settle down to the beneath of the sump and it first come out while draining of lubricant. This value is used to calculate the viscosity of the fluid. Viscosity is the one main property of a lubricant, so for calculation of the viscosity of lube oil the density must be known. Kinematic viscosity is a ratio of absolute viscosity to the density value. That means, whenever density of lubricant changes due to any reason, error occurs in the calculation of both viscosities. Generally, the density of fluid is given in relation with specific gravity, which is the relationship of density to water. The specific gravity of the water is one, so any fluid which is having low specific gravity than the water will be lighter than the water and the specific gravity more than one will be heavier than water. This property of a fluid is crucial for several attributes of a lubricant. As the density of a lubricant rises, the fluid turns out to be thicker [117]. This leads to a rise in the extent of time it takes for particles to hold up out of suspension.

The specific gravity of rust lies between 2.44 to 3.6, so when the oil gets thick, particles of rust and similar contaminant settle out very slower in reservoirs and further areas with reside time in the fluid. The hydraulic systems are much sensitive to contamination, the failure may occur due to the contamination [117]. It is therefore, if the rust particles are in suspension for long time, it can produce silt lock, cavitation and corrosion. The deviation on the density of the oil may create the problems of cavitation in the pump and

orifice, increase the pumping power requirement, increase the stress to pump, and the weak pump ability because of fluid inertia.

According to Fitch, "High-density fluid contributes to better contamination control by aiding in the suspension, transport and removal of particulate contaminants." Since the foreign particles are held in suspension longer time, they are very easily cleaned by filters and other particle-removal systems, thus making it easier to clean the system.

It is significant to note that some lubricants are heavier than that of water. Most phosphate-ester fluids have a specific gravity of more than one. In such cases, water floats on top of the oil. As density increases, the erosive potential of the fluid increases. Not only are solid particles affected by the density of a fluid, but so are contaminants such as air and water. Both of these contaminants have a marked impact on density. Oxidation influences the density of a fluid as well. As the oxidation progress, the density of the oil increase. Overall, density plays a critical role in how a lubricant functions as well as how machines perform. Most systems are designed to pump a fluid of a specific density, so as the density begins to change, the efficiency of the pump begins to change as well [117]. Density of engine oils is a function of engine operating temperature. Its known fact that the density of lubricating oil decreases with rise in temperature [118]. The thermal conductivity and density inside engine increase with running time [118]. K. Vesela et al [119] found that viscosity and density of the engine oil decrease up to 20% for E85 fuel.

CHAPTER 4: RESEARCH METHODOLOGY

4.1 Fuel blend preparation and its stability

There were three fuel blends of different proportion of butanol and diesel prepared on volume to volume basis as per given in the Table 5. The blends were termed B10 containing 10% butanol, B15 containing 15% butanol, and B20 containing 20% butanol. Though, butanol is miscible in the diesel, the additive (hydrofuran) supplied by Energenics Pte. Ltd. Singapore was used to get the homogenous blend while biodiesel was used as a co-solvent to get the stable blends and to maintain the cetane number of the blends. After blending, the fuel blends were tested for the stability. All the fuel blends were contained in the separate tight cylindrical container for 15 days in the open atmosphere. All blends were remained stable and no phase separation was recorded. Butanol has a lower cetane number than that of diesel. Thus, the addition of butanol reduces the cetane number of the blends. Biodiesel helped to compensate the cetane number of blended fuel.

Table 4-1: Test fuel blends volume/volume basis

| Fuel | Proportion |
|--------|---|
| Diesel | Neat diesel |
| B10 | 74% diesel +15% biodiesel + 10% butanol + 1% additive |
| B15 | 64% diesel+20% biodiesel + 15% butanol + 1% additive |
| B20 | 54% diesel+ 25% biodiesel+ 20% butanol+1% additive |

4.2 Physico-chemical property of fuel blends

Physico-chemical properties of diesel and fuel blends were determined as per the ASTM standard. The ASTM standard is given in the Table 4.2

Table 4-2: ASTM Standard test methods

| Property | ASTM Methods |
|--|--------------|
| Fuel Density g/cm ³ | D1657 |
| Viscosity 40 ⁰ C (cp) | D2162 |
| Flash Point(⁰ C) | D93 |
| TBN (mg of KOH/g of oil) | D974 |
| TAN(mg of KOH/g of oil) | D664 |
| Calorific value (KJ/kg) | D240 |
| Metal element in lubricating oil (PPM) | D7740 |

4.2.1 Measurement of calorific value (CV)

Calorific value was measured using Bomb calorimeter according to ASTM D240. Calorimetry is the science of measuring quantities of heat, as distinct from “temperature”. The instruments used for such measurements are known as calorimeters. The calorific value (heat of combustion) of a sample may be broadly defined as the number of heat units liberated by a unit mass of a sample when burned with oxygen in an enclosure of constant volume. Thus the term calorific value (or heat of combustion) as measured in a bomb calorimeter denotes the heat liberated by the combustion of all carbon and hydrogen with oxygen to form carbon dioxide and water, including the heat liberated by the oxidation of other elements such as sulfur which may be present in the sample. The SI unit of calorific value is KJ/kg. Figure 4.1 shows the bomb calorimeter.



Figure 4-1: Bomb calorimeter

4.2.2 Measurement of Viscosity of the fuel

Viscosity of the fluid is the measure of the resistance force of one layer to adjacent layer. Viscosity was measured by fungi lab viscometer at constant speed of 100 rpm. The 200 ml of fuel is taken in the beaker. The spindle attached to the machine was dipped in the beaker containing fuel. The spindle rotates and produces the shear on the fuel. The water bath is connected to the beaker to provide the constant temperature. Figure 4.2 shows the viscosity meter.



Figure 4-2: Viscosity meter

4.2.3 Measurement of density

Density of the fluid is mass per unit volume. The SI unit of the density is given by kg/m^3 . Density was measured with density meter at 15°C . Figure 4.3 shows the density meter.



Figure 4-3: Density meter

4.2.4 Measurement of Flash point of the fuel

Flash point is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material. The flash point temperature was determined in accordance to the standard ASTM-D93 using closed cup tester. Figure 4.4 shows the flash point apparatus.

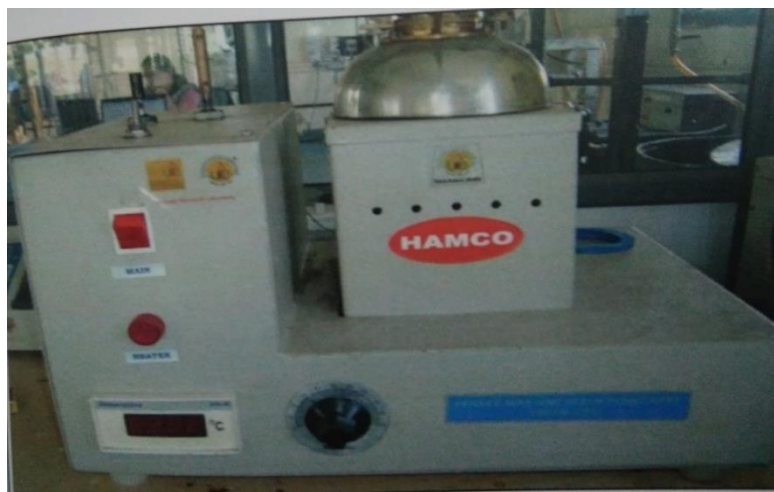


Figure 4-4: Flash and fire point apparatus

Table 4-3: Properties of alcohol compared to biodiesel and diesel

| Properties/Fuel → ↓ | Diesel | Biodiesel | Butanol | B10 | B15 | B20 |
|------------------------------|--------|-----------|---------|-------|-------|-------|
| Density (kg/m ³) | 823 | 890 | 813.3 | 832.1 | 834.2 | 836.4 |
| Viscosity(cp) | 2.51 | 4.26 | 2.21 | 2.52 | 2.56 | 2.58 |
| Calorific value KJ/kgK | 45000 | 35400 | 33110 | 40649 | 37497 | 36180 |
| Flash Point(°C) | 52.5 | 108.7 | 43.3 | 41 | 39.2 | 37.2 |

4.3 Experimental Set up

The experimental set up consists of a Kirloskar make, 5 HP, 4 stroke single cylinder, water cooled diesel engine. The engine is coupled with the eddy current dynamometer. The engine comprises of the spring loaded indicator, air tank, fuel tank and fuel measuring burette. There were four identical engines

installed in common work space in order to maintain the same atmospheric environment of work place. All the engines were operated at a constant speed of 1500 rpm using the different blends of butanol with loading conditions as given in Table 4.6. Test engine setup is shown in the Figure 4.5 and Figure 4.6 shows data acquisition panel. The eddy current dynamometer was used for engine performance determination. Table 4.2 shows the complete engine specification and Table 4.3 shows the dynamometer specification

Table 4-4: Specification of engine

| Technical Specification | | |
|--|------------|---------------------------------|
| No. of Cylinders | - | 1 |
| Bore X Stroke | (mm) | 80 X 110 |
| Cubic Capacity | (Ltr) | 0.553 |
| Compression Ratio | - | 16.5 : 1 |
| Rated Output | kW(hp) | 3.7 (5) |
| Rated Speed | Rpm | 1500 |
| Torque at Full Load (Crankshaft Drive) | kN-m(kg-m) | 0.024 (2.387) |
| Crank Shaft Center Height | (mm) | 203 |
| Specific Fuel Consumption (SFC) | (gm/hp-hr) | 195 + 5% |
| Lub Oil Consumption | - | 0.8% of SFC max. |
| Lub Oil Sump Capacity | (Ltr) | 3.7 at higher level on dipstick |
| Fuel Tank Capacity | (Ltr) | 6.5 |
| Physical dimensions of bare engine (Length X Width X Height) | (mm) | 617 X 504 X 843 |
| Engine Weight (dry) | (kg) | 130 |
| Rotation while looking at the flywheel | - | Clockwise |
| Power Take-off | - | Flywheel End |
| Starting | - | Hand Start |
| Governing | - | Class "B1" |
| Type of Fuel Injection | - | Direct Injection |
| Overloading Capacity of Engine | - | 10% of Rated Output |

Table 4-5: Specification of dynamometer

| | |
|-------------------------|----------------|
| Type | Eddy Current |
| Cooling | Water |
| Load Measurement method | Spring balance |
| Max. Speed | 1500 RPM |
| HP | 5HP |
| Coupling | Tyre |

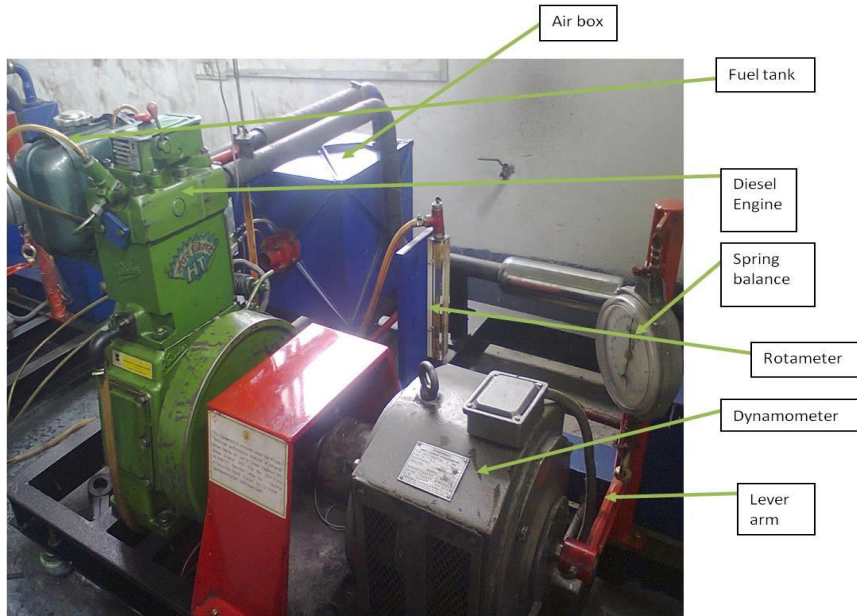


Figure 4-5: Engine Setup



Figure 4-6: Data acquisition panel

4.4 Rheometer

Lube oil is a combination of base oil and different additives. Rheometer (Anton Paar QC rheolab) Austria, type C-LTD80/QC with working temperature range of -20 to 80 °C at 0.5 bar pressure was used to measure the viscosity of the engine oil. Approximately 10 ml sample of oil is taken in the

stationary cup. The cup is connected through the temperature bob Pt100 to measure the variation of the temperature. It is used to carry out the rotational test where the desired speed is preset. Shear rate and the torque acting on the measuring bob due to flow resistance of the sample is measured (shear stress). It shows the measured and calculated values of the speed, torque, shear rate, shear stress, viscosity and temperature. Figure 4.7 shows the rheometer used in the present study.

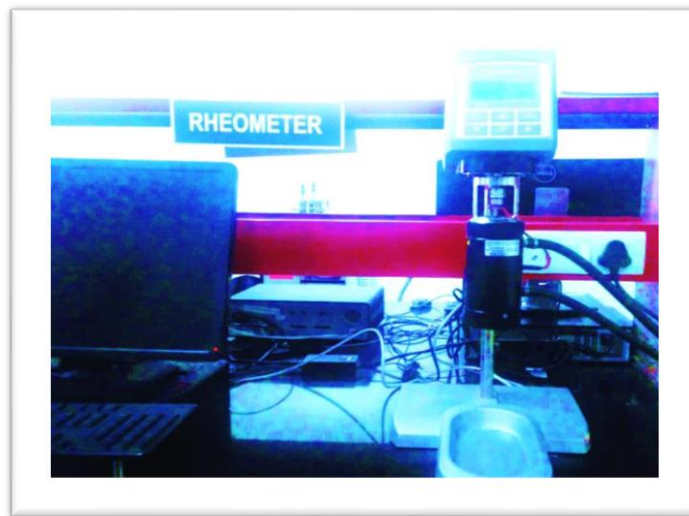


Figure 4-7: Rheometer

4.5 Determination of TBN and TAN

The most important tool for characterization of lube oil is the TBN. TBN is determined by the quantity of acid needed to complete neutralization of lubricant. Total base number is the amount of lube oil alkalinity which specifies the capability to oppose the consequence of the oxidation, temperature and also neutralizes the weak and strong acids. Total Acid Number and Total Base Number were determined by the color indicator titration method. It determines the acidic or basic constituent in the lubricant and petroleum product which is soluble in the solvent of toluene and the isopropyl alcohol. Both used engine oil and new engine oil can have the acidic characteristics such as esters, natural and inorganic acids, phenolic mixes,

lactones, gums, salts of substantial metals, and expansion specialists like inhibitors and cleansers.

This test method gives the indication of the relative changes occur during the operation in the oxidizing conditions. Hydrochloric acid solution is prepared for the titration. 9 ml of concentrated hydrochloric acid is mixed with the 100 ml of 2-propanol in order to get the 0.1M alcoholic solution. While potassium hydroxide solution of 0.1M is obtained by the adding 6g of solid KOH in 1 litre of 2-propanol. And to get the proper dilution, the solution is boiled for 10-15 minute. To determine the acid numbers, the 0.1M KOH solution was added in increments to the solution of lubricant and the solvent and mixed vigorously till the color changes to green or green brown. For determination of base number of oil, 0.1M HCl titrator was used until the green brown color changes to orange [124, 125]. The following formula is used to obtain the acid number.

$$\text{Acid number, (mg of KOH/g)} = [(A-B) M * 56.1] / W$$

Where

A= KOH solution required for titration of the sample

B= KOH solution required for the titration of blank

M= Molarity of the KOH solution

W= Weight of the sample g,

$$\text{Base number (mg of KOH/g)} = [(Em + FM)] * 56.1 / W$$

Where E= HCl solution required to titrate the blank solution ml

m= Molarity of HCl solution

F= KOH required for the titration of the acid number blank ml

M= Molarity of the KOH solution,

W= Weight of sample used g

4.6 Atomic Absorption Spectroscopy (AAS)

Generally, the two spectroscopy methods are used to have the analysis of any fluid. Namely, the atomic emission spectroscopy and atomic absorption spectroscopy. The atomic absorption spectroscopy is based on the principle of atom physics that the light of a fixed wavelength is absorbed by the atom

within the visible region of the vitality range. However, the atomic emission spectroscopy is based upon the principle that the atom emits the light of certain wavelength between the visible and ultraviolet region. The operation of the atomic absorption spectrometry is shown in the Figure 4.8. (a) and (b). In AAS, the atomization of metallic elements is done with the help of oxy-acetylene flame.

The wavelength of the light consumed by the components in the sample is distinguished and evaluated by the spectroscopy [75]. The readied tests for the nuclear ingestion spectrometry are suctioned into the oxy-acetylene fire of the spectrophotometer and the showed absorbance is recorded. In the process, the arrangement is changed over to vapor containing free particles. The radiation normal for the component being checked is transmitted from a light source and coordinated through the vapor. A portion of the iotas scattered in the vapor are consumed to a fitting extent of the radiation bringing about the lessening of the radiation rising up out of the vapor. This decline is estimated by an indicator as the absorbance. The absorbance esteems acquired is utilized to get the convergence of the component by extrapolating from the alignment chart got for arranged control.

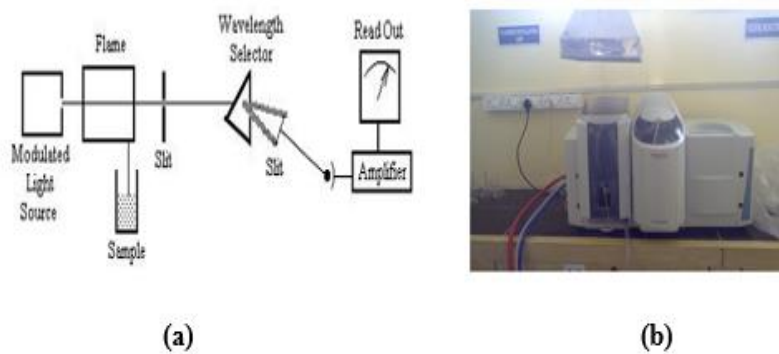


Figure 4-8: (a) Schematic diagram of AAS (b) Actual set up AAS

4.7 Endurance test procedure and plan of engine

As per IS:10000 code, to perform an endurance test, engine needs to be rushed to 32 cycles, each cycle includes 16 hours constant running at rated speed and at different loading conditions as given in Table 4.6. The engine runs initially for 30 minute to warm up and to maintain the constant speed.

After that, the engine is applied 100% load of rating of engine to replicate the harsh driving condition. Sequentially, it is loaded 50% of the rated power (moderate load condition) and given 110% of load to replicate severe loading followed by running on no load condition for 30 minutes. At the end of 16 hours cycle, the engine was stopped for fundamental overhauling and modifications.

Table 4-6: Test cycle plan for Endurance Test

| Load (percent of Rated load) | Running Time (hours) |
|------------------------------|--|
| 100 | 4 (including warm up period of 0.50 h) |
| 50 | 4 |
| 110 | 1 |
| No load (idling) | 0.5 |
| 100 | 3 |
| 50 | 3.5 |

4.7.1 Engine oil characterization

4.7.1.1 Sample collection

Engine oil samples were gathered precisely from each of the four engines using syringe soon after 5 minutes of engine switched off to maintain the homogeneity of oil. The samples were stored in the cool and dry place to keep it safe from the contamination till it was prepared for the Atomic absorption spectroscopy (AAS) analysis. The samples were taken from the engine sump after completion of every 48 hr. These samples were converted into the aqueous solution of 100 ml and subjected to wear particle analysis in the atomic absorption spectroscopy within the 24 hour of sampling. The complete characterization of used lube oil needs a set of the different analysis, such as TBN, TAN, and viscosity, density and wear metals content. Total Acid Number (TAN) and Total base number (TBN) were determined by the titration method while wear metal concentration was determined using AAS. Rheometer is used to measure the viscosity of used lube oil. The collected samples are shown in Figure 4.9.



Figure 4-9: Engine oil samples for analysis

4.7.1.2 Ash digestion and sample preparation

In order to analyze the lube oils for wear concentration, the oil samples were ash digested. 2 grams of oil were weighed in the crucible. After weighing 2 grams of sulfuric acid was added and kept on hot plate at temperature 70-80⁰C for 45 minutes so that the oil get dry. The crucible was now shifted to muffle furnace for 1-1.5hr. The temperature of the furnace is maintained at 550-600⁰C. The ash of the oil was dissolved in the 6ml concentrated HCL and filtered. Finally, 100ml solution was prepared by mixing the distilled water. The calibration curve was obtained from standard solutions of different metal with concentrations ranging from 2 ppm to 10 ppm. All the samples were now subjected to AAS analysis. Table 4.6 shows the ASTM standard method followed. The prepared samples are shown in the figure 4.10.



Figure 4-10: Prepared samples for the AAS analysis

4.7.1.3 Standard dilution for AAS

The quantification of the elemental value of the concentrated metal in the engine oil is made by known quantity of the standard ppm. Standard solution of 1000 ppm is converted in to required lower ppm concentration by dilution in the distilled water. The serial dilution method is the most appropriate method in which the dilution obtained from the previously diluted standard.

Conversion of ppm.

$$C_1 V_1 = C_2 V_2$$

Where,

C1 be the concentration of standard solution (ppm)

V1 be the volume of standard solution required for dilution (ml)

C2 be the diluted concentration needed (ppm)

V2 be the diluted volume needed (ml)

4.7.1.4 Calibration curve

Calibration curve is obtained by aspirating the standard of known concentration. At least, four samples of known concentration required to find the calibration curve. Distilled water is considered as the first point having zero concentration standards. The calibration curve is drawn between the absorbance and the concentration of the known sample. Ideally the curve is expected a straight line. Figure 4.11 shows the calibration curve.

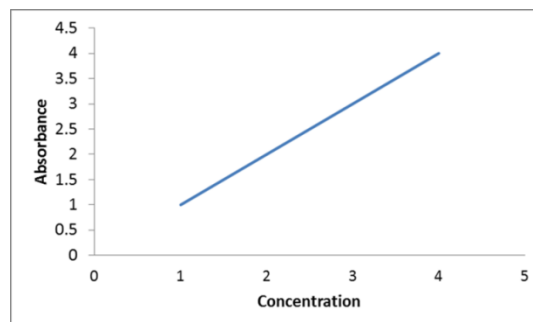


Figure 4-11: Calibration curve

CHAPTER 5: RESULTS AND DISCUSSION

Change in Physico-chemical properties of the engine oil depends on the impact of the butanol and biodiesel in the engine oil when the engine is kept running for quite a while. Also, the engine oil was subjected to the wear analysis. Based on the engine oil analysis; the viscosity, density, total base number, total acid number and wear metal were measured and the engine oil drain interval was decided.

5.1 Viscosity of engine oil

The wear of the engine component depend on the lubricating oil viscosity, consequently, the fuel efficiency. Kinematic viscosity is a quantity of liquid defense from stream and shear under the gravitational force. The viscosity was estimated utilizing Rheometer Anton Paar QC at the temperature of 40⁰C at constant shear rate of 100 s⁻¹. The samples of engine oil were drawn after the every 48 hours of run in order to evaluate the engine oil and engine conditions. The variation of engine oil viscosity with time for the diesel- butanol blends was compared with that of the engine oil of diesel fueled engine as baseline data. Figure 5.1 shows the variation of viscosity of engine oil of B10, B15, and B20 fueled engine together with diesel. Engine oil from the B15 and B20 fueled engine shows nearly equal change 14% and 15% respectively after 48 hours of run due to higher amount of biodiesel present in the fuel which enters to the engine oil while operation. As the usage time increases the viscosity decreases for the 96 hour of run; the engine oil viscosity from the engine fueled with diesel, B10, B15 and B20 shows a decrease of 45.6%, 41.4%, 35.5% and 39.7% respectively. Similarly after the 144 hours of run, the diesel, B10, B15 and B20 shows a decrease of 61.6%, 54.1%, 42.6% and 45.5% respectively. On further use, the viscosity is reducing more such as for 192hours of run diesel, B10, B15 and B20 shows a reduction of 65.3%,

55.5%, 48.65% and 50% respectively. After 288 hour of run diesel, B10, B15 and B20 shows respectively 81.2%, 67%, 53% and 50.9% reduction in viscosity. In this study the viscosity of the engine oil of all engines is found to decrease up to the 288 hours of run. After that viscosity of all the engine oil samples is increased up to 512hours of run. Engine oil from the B10 fueled engine shows more reduction than the diesel fueled engine. Butanol being alcohol has the property of the thinner. So it reduces the viscosity. Engine oil from the B15 and B20 fueled engine showed nearly equal change 14% and 15% respectively due to higher amount of biodiesel present in the fuel which enter to the engine oil while operation. The biodiesel has high viscosity. However, the viscosity of engine oil from B15 and B20 fueled engine shows reduction well above the limitation of oil change. These two engines were fueled with biodiesel and butanol enriched fuel thus show less reduction in viscosity. The viscosity of engine oil reduces with increase in time. During the operation of the engine, the cylinder temperature and pressure increases. At high temperature, higher chain hydrocarbons convert into the small chain hydrocarbon. The viscosity of lubricating oil changes with the temperature. As the temperature increases, viscosity reduces. The fuel dilution in the engine may degrade viscosity. Also the additive depletion occurs in long time use of lube oil resulting in lower the viscosity. As the butanol content increases in the blend, its viscosity increases. The hygroscopic nature of butanol may also be responsible for the increase in viscosity due to emulsification of engine oil. The cetane number of the butanol is not as much as that of diesel fuel which brings down the chamber temperature and subsequently, deficient ignition. Because of incomplete combustion soot formation takes place in the engine oil which increases the viscosity. Stodola J. et al [102] have proposed the three stage oil degradation i.e. scavenging, operation and balance (equilibrium). In scavenging; the physico-chemical properties of oil changes by 25%. It is the best force of degradation of oil. In second stage, a large number of km of activity, where the physical and substance parameter of oil changes almost by 50%, the unequivocal factor of stage two of debasement is general state of the engine, particularly mechanical state of friction and fixing surfaces. Lastly the balance (equilibrium) stage happens when recovery forms to wipe out the

advance of degradation of oil. Viscosity estimation of the engine oil gives data of oil thickening because of residue pollution entrance, oil oxidation, and fuel dilution and defilement with fuel, water or coolant. The viscosity is decreased during the time span of 150 h of engine run as compared to initial oil viscosity. It has been observed that the viscosity decrease is 21% for the SAE20W40. Kinematic viscosity of engine oil may diminish at the outset because of shearing of the viscosity index improver and begin expanding later because of oil oxidation. Other studies have reported 18% decrease in kinematic viscosity with the utilization of biodiesel/synthetic lubricant combination [67]. This is due the fact that butanol and biodiesel both are having high heat of vaporization causing some part of injected fuel to remain unburnt and scrapped by the piston up to the sump to mix with the engine oil thereby increasing the viscosity. Increase in operating time provides the gap for the engine blow by gases. Soot contained in the blow by gas gets mixed with engine oil leading to increase in the viscosity. It is a general consideration that whenever the viscosity increase or decrease by 25% of the unused oil viscosity, the oil must be replaced by new engine oil. Many researchers have studied the endurance test of diesel with biodiesel fuel and they changed the engine oil with new oil after the 100hr. P.R. Wander et al [127] run the engine for the 1000 hours after fueling the engine with castor oil methyl esters CME 100, soya methyl ester SME100 and diesel. They observed an increase in the viscosity of the engine oil the usage time. S.A. Adnani et al [128] found that the useful life of the oil is 100 hour of run. This is due the fact that lower viscosity allows the boundary lubrication between the piston ring and cylinder but fails to provide the sealing and increase the blow-by leading to fuel dilution in the sump.

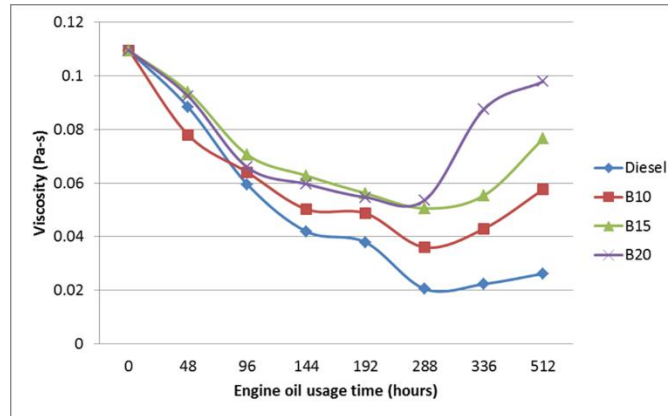


Figure 5-1: Viscosity variation of engine oil of B10, B15, and B20 fueled engine compared to diesel.

5.2 Density of engine oil

Density is a primary property of every fluid whether gas or liquid. It is the measure of the mass of a substance with respect to a perceived volume. Lubricants generally have lesser density than water. The object with lower density than the water will float in water. The moisture contained in the lube settle down to the beneath of the sump and it first come out while draining of lubricant. Density of the engine oil from all engines fueled with diesel, B15, and B20 gets reduced by 0.8%, 0.5% and 0.8% respectively while that of B10 fueled engine gets increased by 1% after 48 hours of run when compared with the unused engine oil. Density decreases slightly for all the engine oil up the complete test. The trends of viscosity and density have been found similar. Density of the engine oil from the diesel fueled and B15 engine decreases up to 144 hours of run while that increases slightly for engine oil from B10 fueled engine. The density of the engine oil from the B20 fueled engine is found to decrease drastically initially but increases continuously afterwards. The density of engine oil from the B10 fueled engine increases continuously till 336 hours of run. The density of diesel fueled engine oil and B15 fueled engine oil slightly increases up to 192 hours of run and decreases afterwards till 288 hour of run. The density of the all engine oils increases up to the completion of the test i.e. 512 hr. Density of the engine oil of the B15 fueled engine was observed more stable than the other three engine oil. Density of this engine oil from B15 fueled engine increases continuously but with very small change. Density of engine oil changes with the temperature; generally,

when temperature increases the density decreases. Whenever, the engine oil takes part in the operation of the engine, it subjected to high thermal stress leading to decrease in density. The fuel dilution in the engine oil is also responsible for the lowering of the density. The butanol and the biodiesel both are oxygenated fuel which provides the oxygen for proper burning of the fuel thus, temperature increases and as lubricant gets closer to the high temperature zone of the engine, it losses the density due to high heat. At the same time, some part the biodiesel remain unburnt due to its high heat of vaporization as compared to the diesel, thus unburned biodiesel and butanol mixed in the sump engine oil which increase the density of the oil. It is clearly observed from the figure that in the initial 96 hours of run of engine, density is decreasing but as the operating time increases, density of engine oil increases. This is due the fact that the wear of engine component increased with operating time thus, more passage way may be created for the engine blow – by. The exhaust gas contains the carbon particle which generates the soot. The soot particle increases with operating time and get mixed with engine due blow-by. Due to the soot in the engine, oil density increases after 196 hours of run. The oxidation of the engine oil in the existence of oxygen provided by the biodiesel and butanol thicken the engine oil. Kinematic viscosity depends on density of engine oil [129]. The erosive potential of the lubricant increases with the increase in density [117]. Ryan James Clark has found that the accumulation of the soot and contamination and oxidation by product degrades the engine oil and intensify the bulk density of the engine oil [120]. Density is decreased due to thermal expansion of the lubricating oil. Butanol has alcoholic property which may dilute the engine oil and reduces density. The density of the engine oil of B15 fueled engine remains higher among all engines. The density of engine oil of B10 and B20 fueled engine were measured lower than that of the diesel fueled engine oil. The figure 5.2 shows the variation of the density.

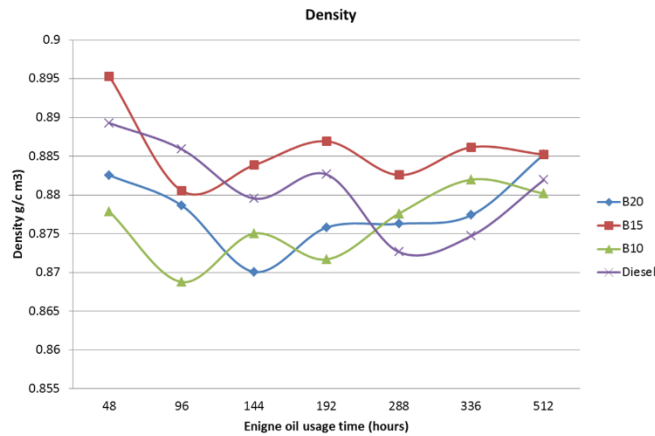


Figure 5-2: Density of engine oil of B10, B15, and B20 fueled engine as compared to diesel.

5.3 Total Base Number (TBN) of engine oil

Total base number is a measure of ability of lube oil to counter the acid attacks generated in the lube oil during the operation. Figure 5.3 shows the total base number with the usage time. TBN is provided in the lube oil to resist the acid formation or to neutralize the acid and prevent the engine component from the corrosive wear. The value of the TBN in the engine oil varies to OEM. OEM mentions the oil drain interval based on the Sulphur concentration in the fuel used in the engine. The engine oil drain period recommended by OEM is 200 hours for engines used in the present study. We cannot follow the same recommendation for 15ppm Sulphur fuel and 1000ppm Sulphur. TBN varies from 6-70 mg KOH/g; the higher total base number is used for the marine engine in which higher Sulphur content presents. Generally, the TBN is taken 6-10 mg KOH/g for the passenger car. Corrosive wear occurs due the oxidation of the oil when it gets exposed to high temperature generated in the engine at the time of combustion. As shown in figure 5.3, the TBN of engine oil reduces with increase in usage time as well as with increasing butanol additions in the blends. This is due to the fact that the alcohol possesses the acidic property and hygroscopic in nature. Moisture promotes the rust formation and corrosion of the engine component. It also imparts an adverse effect on the additive material by precipitating the additive. Butanol promotes the oxidation of lubricating oil and reduces the load capacity of oil. Thus, both of the properties of butanol contribute in degradation of the lube oil which

results in the decrease of the base number. If the total base number (D-4739) of engine oil reduces to one third of that of the unused engine oil, the oil must be drain [125]. Also, if TBN reduces to 50% of that of the unused oil, then it should be replaced (ASTM D445) [122] [130]. Charlotte Besser et al [48] have performed the chassis dynamometer test in which engine oil was contaminated by the addition of known quantity of acetic acid in order to evaluate the effect of the acetic acid on the properties of engine oil and corrosion effect. Ethanol produces acetaldehyde and acetic acid in combustion [48]. They found that it is corrosive to engine components made of iron and copper. The total base number of the engine oil is decreased to 1.3 mg of KOH/g of oil in first 40 hours of run. Figure 5.3 shows the variation of the TBN with usage time. From the figure, it is seen that the TBN reduces to 5 nearly in 288 hr of run so, the depletion rate of the additive is slower for the engine oil of diesel fueled and B10 fueled up to the 192 hr however, the TBN of the engine oil of B15 and B20 fueled engine decreases continuously. The engine oil must be changed after 100 hr based on the TBN but this is not the only decision parameter. There are other parameter such as wear, TAN, viscosity and density of engine also to be carefully taken care of. S.A. Adnani et al [128] found that TBN of engine oil reduces to 7.5 from the 14.5 mg of KOH/g of oil after 120hr of run so they drain the oil after 100 hr of run.

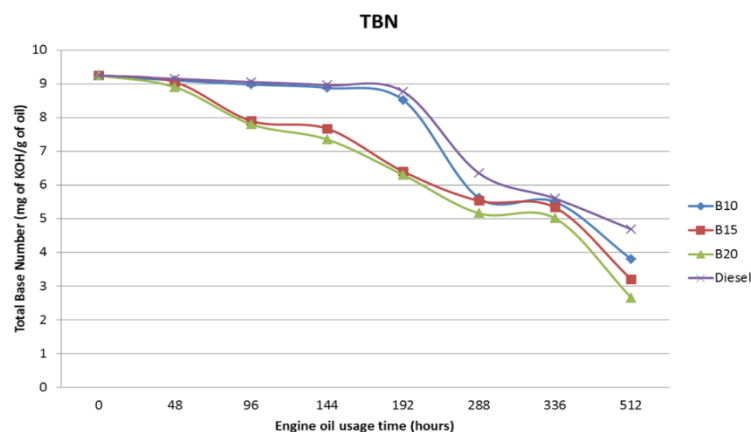


Figure 5-3: Total base number of the engine oil of B10, B15, and B20 fueled engine compared diesel

5.4 Total Acid Number (TAN) of engine oil

Total acid number is a measure of the acid that remains un-neutralized in the lubricating oil. TAN increases with the acidic contamination and oxidation by product. It is a count of both strong acid and weak acids and increases with usage time. Figure 5.4 shows the variation of total acid number with the usage time. One can observe that acid number increases with the time for all the butanol- diesel fuel blends. In the presence of oxygen, which is omnipresent in most lubricating environments, hydrocarbons making up the base oil can react to form carbonyl-containing products (primary oxidation products), which subsequently undergo further oxidation to produce carboxylic acids (secondary oxidation products), resulting in increased TAN values. Oxidation of base oil generates the acids in the lubricating oil and base detergent fails to neutralize the acid. Further use of oil increase the acid content. As the butanol and biodiesel content in the blends increases, the total acid number increases. This is due to the fact that the butanol and biodiesel provides more oxygen in the form of unburned fuel which dilutes the engine oil and provides more oxygen for oxidation of engine oil. The butanol itself has acidic nature which can result additive depletion and oxidation of base oil thus, increase the TAN. The main concern with the presence of alcohol and water is the formation of acid that can be formed in the oil at very low activation energy levels and does not require high temperatures as necessary for acid byproducts from the oxidation or nitration process. Unburnt alcohol reacts with oxygen and oxidizes further and forms acetic acid (synthetic carboxylic acid, CH_3COOH). The presence of acetic acid and water in the oil bears a high risk of engine corrosion. Corrosion increases the wear. Reduction in the TBN increases the TAN i.e. engine oil acidity increases with increase in butanol content in the fuel. Acid no of 4mg of KOH/g is highly corrosive [128] which indicates that the oil should be drained. From the 5.4 it is seen that the TAN of all the oil reaches to 4 between 288-336 hr of run.

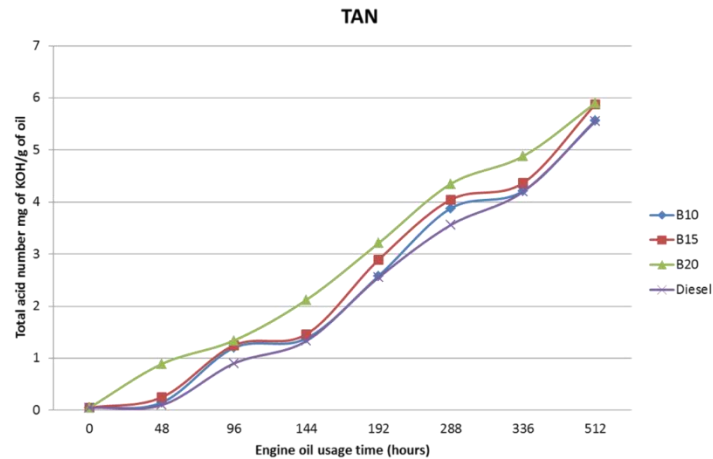


Figure 5-4: Total Acid number of the engine oil of B10, B15, and B20 fueled engine compared diesel

5.5 Wear analysis

Figure 5.5 and 5.6 Shows the variation of iron and copper concentration in the engine oil with usage time respectively. One can observe from the figures, that both the iron wear and copper wear increases with the time and butanol content in the blends. Iron wear is very high for the B20 fueled engine as compared to diesel fueled engine; the iron wear is 384% higher than the diesel fueled for first 48 hr. This is due to the fact that the fuel contains 20% butanol in the blend which promotes the acid attack to new engine. While the iron wear of B10 fueled engine is 14.65% less than the diesel for the 48 of run and closer to the diesel fueled engine for 96 hours of run. However, B15 is 33% higher for 48 hr and 11% higher for 96 hour of run than that of the diesel fueled oil. The iron wear for B20 fueled engine is 101% higher for 96 hours of run. This is due to the fact that the new engine wears fast in wear-in period. Similarly, it is clear that the iron wear for B10, B15 and B20 is respectively 6%, 28% and 114% higher than that of the diesel fueled engine for 144 hour. For 192 hours, the wear is found to be respectively 21%, 86%, 140% higher than the diesel. But when engine runs in the constant wear period, the iron wear is 4.7%, 8% and 36.6% higher for B10, B15 and B20 for 288-336 hour of run. Because of very high wear, B20 fueled engine has got failure as its piston was torn down. However, the B10 and B15 can be used as fuel in the engine without any difficulty. The range of maximum iron in the engine oil is 42 ppm. Wear particle concentration is a one of the parameters by which the

oil change period is decided. Iron wear may be contributed by the piston liner, valves, and engine head while copper wear is contributed by the bearing. The piston liner and the piston ring experience the maximum loading and temperature of combustion. The sliding contact between the piston rings and liner undergoes all the lubrication conditions such as hydrodynamic, boundary and mixed lubrication. In boundary lubrication, there is metal surface contact between the components, thus initiation of wear occurs from this lubrication. Further, the wear particles are imported in the sump with lubricant from the engine components. In hydrodynamic lubrication; once the wear generated in the lubricant and recirculated to the engine, the wear particles interact between the mating surface and it creates the three body abrasive wear which further increase the wear. Butanol-diesel blended fuel has shown more iron wear than that of diesel fuel. Butanol contains inbound oxygen which improves the combustion, but at the same time oxygen helps to oxidize the lubricant base oil thus, results in increase in wear. The anti-wear additives deplete due to oxidation and losses the property due to which wear of components increase. The effect of butanol is more dominant than the viscosity of blends.

Copper wear is slightly less than the iron wear for all the fuel blends; this may be the less contributing component in the engine. There is a fine thin film developed in the journal bearing and crankshaft. The wear of engine component also increases due to hygroscopic property of butanol, which promotes the corrosion of components. Figures 5.5 and 5.6 show the iron and copper wear for diesel, B10, B15 and B20 respectively. Copper wear is less than that of iron for the fuel blends. Iron wear increases for 288 hours of run for B10. Similar results were found by the P.R. Wander et al after 1000hr endurance test when fueling the engine with biodiesel. They used to change the engine oil after every 100 hr. Similarly Matthew L. Basinger [122] operated the diesel engine fueled with the WVO (waste vegetable oil) to perform the longevity test of 500 hours. He changed the engine oil at every 100 hour. Iron is contributed by cylinder wall/liner, valve shafts, piston ring etc. Copper may be contributed by bearing and bush wear and may be high if the engine has a copper oil cooler [131]. Wear of engine component may occur due to the agglomeration of the soot of higher dimension than the oil -

film thickness which interrupt the lubricant to enter between the contact [132]. Also, the three body wear due to soot may occurred if the soot particles trapped between the two mating surfaces. Generally, soot is soft when agglomerates but as an individual particle it is hard enough to wear the surface [132]. Abhishek Sharma et al have found that the iron and copper wear increases as compared to diesel when engine fueled with JMETHP20 (80% Jatropha methyl-ester +20% tyre pyrolysis oil after the 100 hours durability test [78].

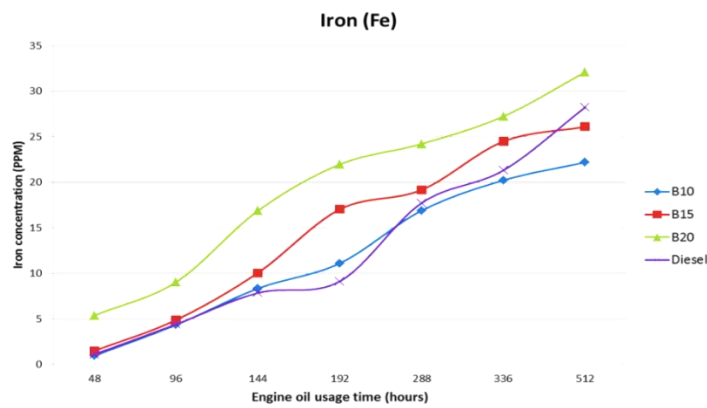


Figure 5-5: Iron concentration in the engine oil of B10, B15, and B20 fueled engine compared diesel.

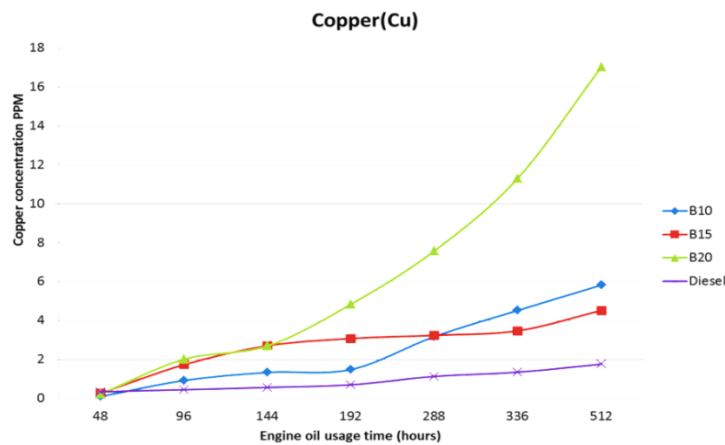


Figure 5-6: Copper concentration in the engine oil of B10, B15, and B20 fueled engine compared diesel

5.6 Visual inspection of engine component

5.6.1 Piston

After the completion of 512 hours run, the engines were opened and the vital part were carefully inspected. The piston of B20 fueled engine was found broken and also the piston ring broke down. As we can see from the figure 5.7 (c), the piston of the B20 fueled engine is broken down. The failure of the piston and the piston ring may occur due to the high temperature generation in the cylinder or due to very high viscosity of the engine oil leading to very high friction. Due to high friction and improper lubrication, the heat is generated and the cylinder and piston ring may be subjected to starvation of the lubricant and boundary lubrication. High temperature in the engine causes overheating, burning of cylinder head gaskets and cylinder liner ferrules, reduction in lubrication oil viscosity and engine seizure. While low lubrication oil viscosity leads to friction, overheating and engine seizure, high lubrication oil viscosity leads to choking of filters, oil starvation and, engine seizure. Low engine temperature leads to high fuel consumption and incomplete combustion [132]. The endurance test for this study involves running a diesel engine with nine test fuels and analyzing the engine's endurance characteristics. The test fuels used were; fossil diesel, and blends of diesel and jatropha biodiesel of blends range 20%, 30%, 40%, 50%, 60%, 70%, 80% and 100%, and the endurance characteristics analyzed were; engine operating temperatures and, lubrication oil and blow-by. They found hard run for 80% and 100% blended fueled engine [132]. The viscosity of oil increases rapidly for the B20 fueled engine and the highest iron wear is observed for the B20 fueled engine. The heat dissipation from the engine is reduced due to higher viscosity of the engine oil, thus, ring sticking may occurs. Excessive carbon on the piston crown is found on B20 fueled engine. Due to carbon particles, soot is generated which increases the wear. While wear of B10 and B15 fueled engine is normal, the weight loss of B15 fueled engine cylinder liner was found higher than the diesel and B10 fueled. The lowest mass loss has been found for diesel fueled engine. Figure 5.7(a), (b), (c), and (d) shows the piston of B10, B15, B20 and diesel fueled engine respectively.

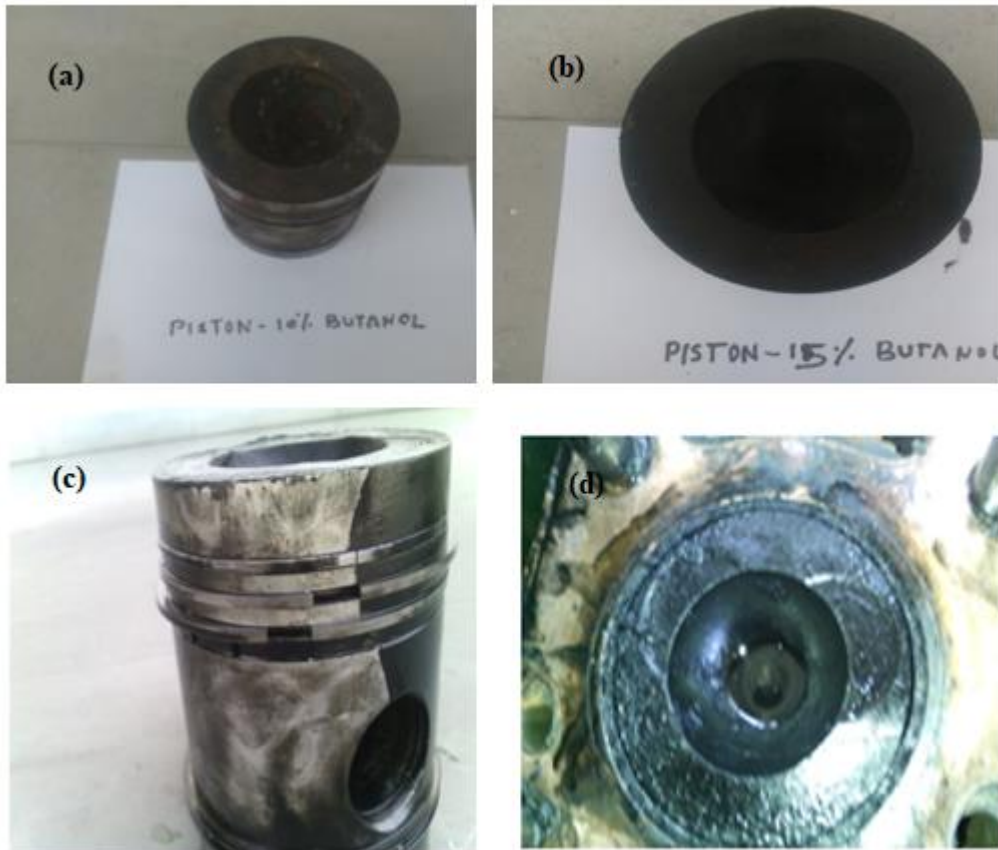


Figure 5-7: Condition of piston of different engines after 512 hours run (a) Piston of B10 fueled engine (b) Piston of B15 fueled engine (c) Piston of B20 fueled engine (d) Piston of diesel fueled engine

5.6.2 Mass loss of cylinder and piston rings

The assembly of the piston ring and piston with the nomenclature is shown in the Figure 5.8. The load bearing surface (piston skirt) is responsible to hold the piston and cylinder properly aligned. The piston land and piston skirt bear the side load when the connecting rod is in the angular position with the axis of the cylinder. The ring governs the lubrication between the cylinder and different surface of the engine piston. There are two type of piston rings used in the engine; the compression and the oil rings. This ring performs the clearance and sealing of the piston and cylinder to minimize the loss of gas pressure of the engine due to blow by, provides the appropriate lubricant to the cylinder for bearing of the high thrust load at the high speed and also, regulates the oil consumption within the acceptable limit. It also controls the temperature of the piston by helping in the heat transfer from the cylinder wall to the coolant. The chromium plating is used to provide the wear resistance to

the outer ring surface [81]. The wear of the piston ring is different for the individual rings. The top ring is nearer to the combustion zone, subjected to the high pressure and due to that, higher wear is generated on it. The pressure drops with distance from the top ring, thus less wear in the bottom rings [122]. As the piston rings degrade due to the wear, the constituent material may be seen in the lubricating oil. The rings may be changed after the careful measurement of the mass loss. The mass loss of cylinder is shown in Figure 5.9 and the mass loss of piston rings is shown in the Figure 5.10.

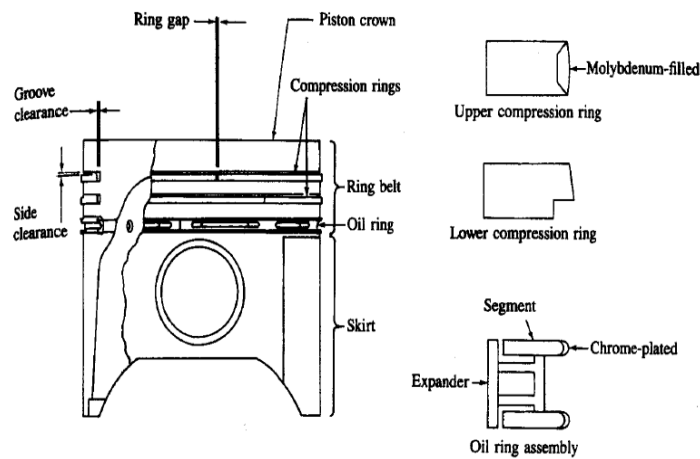


Figure 5-8: Typical piston ring and piston ring assembly [81]

The engines were opened and cylinders were weighted carefully. It is observed that the highest weight loss occurs in the B15 fueled engine among the three cylinders such as diesel fueled, B10 fueled and B15 fueled. Since the B20 fueled engine was broken, we did not measure its weight. The engine wear of B15 fueled engine is higher than the other engine which is proof of the higher mass loss of the engine.

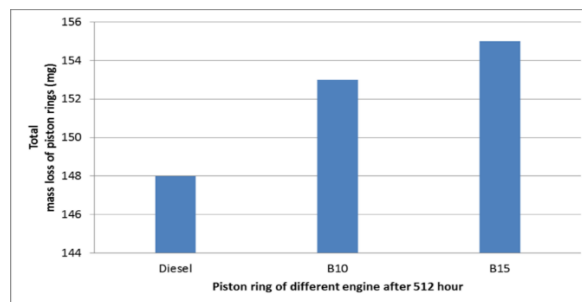


Figure 5-9: Mass loss of the piston ring

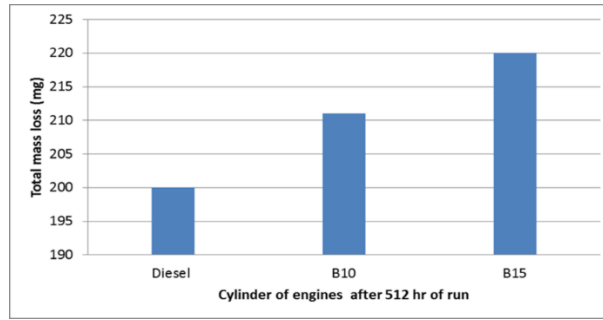


Figure 5-10: Mass loss of cylinders of diesel, B10 and, B15 fueled engine

5.7 Determination of the oil drain interval

The engine operational conditions cause chemical degradation of engine oil with increasing time period. There are different factor because of which chemical structure of the oil changes. The unwanted changes in the chemical properties of engine oil can lead to reduction in the performance of the engine and may cause failure of the engine component. It is therefore, the periodic monitoring of the engine oil property is required. The health monitoring of equipment and optimization of the lubricant uses can be done by the engine oil analysis. The engine oil undergoes different environmental stress and lead to thermo-oxidative degradation of its base stock [129]. The engine oil degrades slowly in the initial period of running due to preventive action of the additive presents; but the degradation happens rapidly whenever the additives get exhausted. The degradation of additive packages can be understood by changing physical and chemical property of the engine oil. The OEM recommends the oil drain period of engine and appropriate engine oil. Early change of engine oil increase the maintenance cost of the engine, while use of engine oil higher than the OEM recommendation may lead to catastrophic failure of the engine. The selection of oil drain interval requirements varies for different engines based upon the operating environment. Tung, et al.[84] have defined four different automotive engine operation/service regimes, each impacting the lubrication oil differently: easy freeway, high-temperature high-load service, taxi service, and extreme short-trip service at low outside temperatures [84]. In endurance test method (IS: 10000), the loading condition given in the Table 4.6 gives the variation of the driving conditions. To

determine the oil drain interval for engine operated with diesel-butanol, different aspects of the engine oil parameter were clearly understood.

Viscosity of engine oil from the all engines reduces with the time but increases with butanol in the fuel. The general rule to change the engine oil is whenever the oil viscosity goes down to 50% of the original oil. The viscosity of the B10 and B15 fueled engine oil is reaching to its 50% value between the 144-192 hours of run while for the diesel fuel, the viscosity reaches in 96 hour. Since change in viscosity of engine oil is because of the change in chemical property of oil the viscosity reduces basically due to the additive depletion; the viscosity modifier additives may deplete fast in the diesel fueled engine. So, the small quantity of the butanol (10-15%) and biodiesel (20-25%) by volume can help the engine to extend the oil drain interval. Viscosity increases after 192 hours of run till 512 hours which is again useful for the better lubrication of engine but higher percentage (20%) of the butanol was problematic for engine endurance. So, the oil drain interval can be considered after 100 hours of run for the B10 and B15 fueled engines. Researcher S.A. Adnani et al [127], suggested the useful life of the oil 100 hour for the diesel fuel. P.R. Wander et al [126] also changed the engine oil after the 100 hour of run when engine fueled with SME and CME. Similarly for the diesel- butanol blended fuel we can recommend the oil drain interval up to 100 hours. A.K. Agrawal [61] found that using biodiesel in the engine improves the viscosity.

Density of the lubricant is defined as the mass per unit volume. Higher density of fluid can help in the lubrication of the mating surface. The kinematic viscosity of the fluid is a ratio dynamic viscosity to the density of the fluid. So, the density of fluid is directly proportional to dynamic viscosity as we can see from the Figure 5.2, the density and viscosity follow the same trend with the blended fuels. The best way to find the optimal time of oil drain interval is based upon the TBN and TAN. Generally, TAN increases and TBN decreases with the usage time. The point where TBN meets with TAN is optimal point to change the engine oil. There is an acid formation in engine oil during the operation. The other rule to change the oil is when TBN reduces to 50% to that of the unused oil. From the figure 5.3, we can see the TBN of the engine oil of B10, B15 fueled engine is reduce fifty percent of its original value after 336

hours. Total acid number (TAN) of oil increases with usage time of the oil. The alkalinity is provided in the engine oil for neutralization of acid. To provide the alkalinity to the engine oil, the alkaline detergents (sulfonates, phosphonates or alkyne) additives are used and it is characterized by the Total base (TBN) in mg of KOH/g of oil. During the engine operation for long time the detergent degrades and lose the neutralization property that results in an increase in the acidity of the oil. Decrease in TBN and increase in acidity is an indicator of the oil drain. The oil should be changed whenever the TAN reach to 4 mg of KOH/g of oil [2]. From the Figure 5.4, we can see that this value of TAN reaches between 288-336 hours. One of the best ways to determine the optimal oil drain interval for the engine and equipment's is comparison of the total base number and total acid number. TBN decreases with usage time, and TAN increases. The optimal point can be obtained the intersection of the both curves as we can see in the Figure 5.11 which shows the variation of TBN and TAN with usage time for diesel fueled engine. It can be observed from the Figure that the TBN curve intersect the TAN curve between 336 to 512 hours of run. OEM also recommends the oil drain interval 500 hours for diesel fuel. Figure 5.12 shows the variation of the TBN and TAN for the B10 fueled engine and Figure 5.13 shows the variation of TBN and TAN for B15 fueled engine oil with time. From both figures we can see that the curve intersect nearly 400 hour of run for both engines which is less than the OEM recommended time interval. So, being on safer side and watching the impact of all results it is recommended to change the after the 100 hours of run. Similarly H. Kaleli et al [129] had found that the engine oil to be replaced after 390 hour for the diesel fuel.

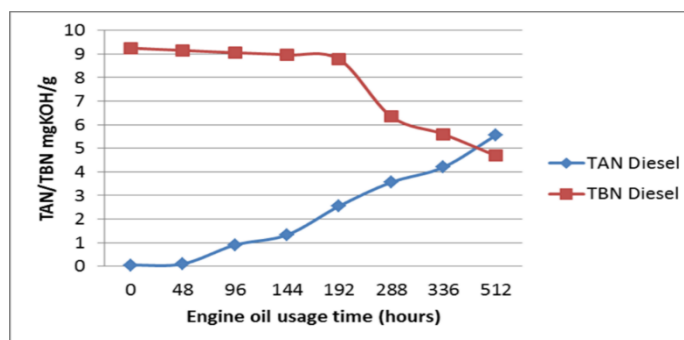


Figure 5-11: Variation of TBN and TAN of engine oil of diesel fueled engine

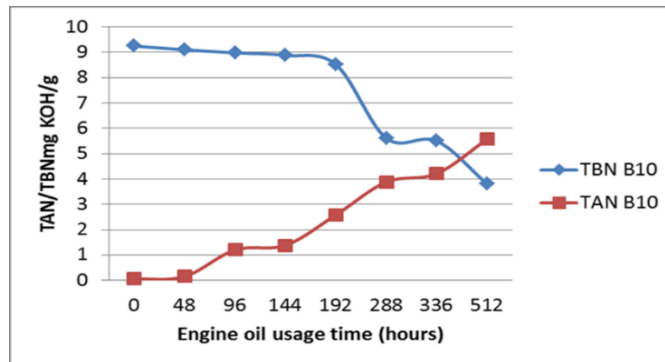


Figure 5-12: Variation of TBN and TAN of engine oil of B10 fueled engine

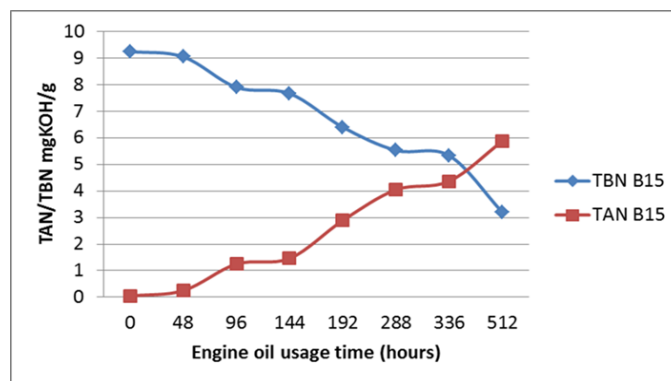


Figure 5-13: Variation of TBN and TAN of engine oil of B15 fueled engine

The wear of engine once occurs, it works as a catalyst for oxidation of the engine oil. From the wear analysis it can be seen that iron and copper concentration for B10, B15 is within the limit or closer to diesel fueled engine. While for B20 fueled engine it increases very rapidly throughout the 512 hour duration.

Even though the TBN seems to be more stable. Hence, the oil drain for B10, and B15 fueled engine can be suggested after 100 hr. while the B20 fueled engine failed within the considered working environment.

CHAPTER 6: CONCLUSIONS AND FUTURE SCOPE

The 512 hour endurance tests on four similar engines were performed. The engines were fueled with diesel- biodiesel- butanol blends containing 10%, 15% and 20% butanol termed as B10, B15, and B20 respectively. After the completion of 512 hour of the engine operation with the blended fuel, the used engine oil was analyzed for the change in the properties (viscosity, TAN, TBN and Density) and wear (Iron and copper) concentration. The visual inspection of the engine components was also carried out. Following conclusions have been drawn from this work:

1. The viscosity of the engine oil from all the four engines initially decreases in the running in period of engine. The viscosity of engine oil of diesel fueled engine reaches its limiting point within 96 hours of run while that of the B10 and B20 fueled engine oil reaches between 144-196 hours of run.
2. The total base number of the all engine oil samples reaches its limiting value between the 288-336 hours of run. The total acid number of engine oil samples from B10 and B15 fueled engine reaches the limiting value after 288 hours.
3. The density of engine oil initially decreases and then increases during endurance test for all the engine oil samples. Density variation is very similar to viscosity variation.
4. Wear in blended fueled engine is higher than that in the diesel fueled engine. Engine wear increases with usage time as well as with increasing butanol content of the blends. However, the iron wear is higher than the copper wear due the less contributing components of copper material in the engine.

5. Engine oil degrades because of the contamination which occurs due to wear metals, fuel dilution, oxidation, external particle ingress and blow-by gases containing the unburned butanol and biodiesel. Butanol increases the oxidation of the engine oil by contributing more oxygen.
6. The mass loss of the cylinder of B15 fueled engine is higher than the diesel and B10 fueled engine. The total mass of the piston rings was found higher for the B10 and B15 fueled engine than the diesel-fueled engine, which is as in agreement to higher concentration of the iron and copper in the engine oil of B10 and B15 fueled engine than that of diesel-fueled engine.
7. The drain period of engine oil is dependent on different parameters of engine oil and visual inspection of the engine components. The dominant parameters are viscosity, TAN, TBN and wear. Based on all result of the engine oil analysis and visual inspection, a drain period of 100 hours is suggested for engine oil of B10 and B15 fueled engine.
8. There is no operational problem with diesel- butanol blends up to the 15% of butanol. However, the higher percentage of butanol creates durability problems as the B20 fueled engine is found to have broken piston, piston ring and bearing after the test. Finally, it is concluded that butanol has potential to be used as a blend with diesel without any modification in existing diesel engines.

6.1 Future Scope

1. Engine oil analysis is an important tool to evaluate the engine conditions and health of the machinery. There are two types of condition monitoring of the engine oil; online and offline. The method adopted for the present study is offline monitoring. Online monitoring can be performed for analysis as future work.
2. In the present study, the B20 fueled engine was broken down. Complete case study of failure of the engine could be the research area for assessment of root cause of the break down.
3. In this study, the fuel blends were prepared on volume basis. Since butanol has lower cetane value, biodiesel is mixed in the blend along

with one percent of the additive (hydrofuran) for getting homogenous blend. The results were discussed only on the basis of the properties of butanol and biodiesel. The effect of additive on the combustion of blends and engine health may be the extension of this research work.

4. In this present study, the concentration of wear particles was measured using the AAS but the wear debris cannot be detected by this instrument. The larger particles may also be appeared in the engine oil and their effect on engine oil degradation and engine wear can be the subject of future study.
5. The experiments can be performed with any of the pollution control device like Exhaust Gas Recirculation (EGR), Diesel Particle Filter (DPF) and the effect of these pollution control devices on engine oil degradation and engine wear may be studied for same fuel blends as used in the present study.
6. Different engine oils with different viscosity grades can be analyzed with the same fuel blends for the selection of the best lubricant for the butanol blended diesel engines.

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List of publications

1. Santosh Kumar Kurre, Shyam Pandey, Rajnish Garg and Mukesh Saxena, Condition monitoring of a diesel engine fueled with a blend of diesel, biodiesel, and butanol using engine oil analysis, , Biofuels, vol. 3-4, 2015.
2. Santosh Kumar Kurre, Rajnish Garg and Shyam Pandey (2017) A review of biofuel generated contamination, engine oil degradation and engine wear, Biofuels, 8:2, 273-280, DOI: 10.1080/17597269.2016.1224291
3. Santosh Kumar Kurre, Shyam Pandey, Rajnish Garg, Mukesh Saxena, Effect of butanol on performance and emission analysis of a compression ignition engine fuelled with Diesel –Butanol blends presented in national conference. 24 NCICEC-2015, on 30oct- 1st Nov. 2015, at university of petroleum and energy studies, Dehradun, India

CURRICULUM VITAE



Name: Santosh Kumar Kurre
Current Address: D/23/8, Raghav Vihar, Premnagar, Dehradun,
Uttarakhand , India Contact- 8126718619, 844949388

Current Organization: University of Petroleum and Energy Studies, Dehradun,
India, since September, 2010

Education:

- B.E (Mechanical Engineering), Pt. Ravi shankar Shukla University Raipur, 2002
- M.E.(Tribology and Maintenance engineering) , SGSITS, Indore, 2004
- Ph.D. Pursuing, UPES, Dehradun

Position: Assistant Professor(SG), Department of Mechanical Engineering, UPES, Dehradun

Professional experience: Teaching, over 14 years in various Engineering colleges.

Areas of Specialization: Engine tribology, Biofuels, Lubrication

Professional Affiliation: TSI, ISTE

Publications:

- I. Santosh Kumar Kurre, Shyam Pandey, Rajnish Garg & Mukesh Saxena(2015): Condition monitoring of a diesel engine fueled with a blend of diesel, biodiesel, and butanol using engine oil analysis, Biofuels, DOI: 10.1080/17597269.2015.1081763
- II. Santosh Kumar Kurre, Rajnish Garg & Shyam Pandey (2017) A review of biofuel generated contamination, engine oil degradation and

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- III. Santosh Kumar Kurre, Shyam Pandey, Rajnish Garg & Mukesh Saxena (2015): Experimental study of the performance and emission of diesel engine fueled with blends of diesel–ethanol as an alternative fuel, Biofuels, DOI: 10.1080/17597269.2015.1078561
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Personal profile:

Father’s name : Late Devkaran Kurre

Date of Birth :15-10-1976

Nationality :Indian

Sex :Male

Marital Status : Married

Permanent Address : Vill- Sonpairy, P.O.-Godhi, Distt- Raipur (C.G.) 492101