Chapter-1

Introduction

This chapter explains the fundamentals of the tribology, lubricants and lubrication mechanism, additive, and their function. Further, chapter highlights the importance of green tribology and green lubrication, and also gives an overview on lubricant about the International and Indian scenario.

1.1. Tribology

Tribology is originated from the Greek word *Tribos* that means rubbing. *Tribology* is the branch of science that deals with friction, wear and lubrication between dynamically mating surfaces. It is a multidisciplinary branch that incorporated with physics, chemistry, material science and various branches of engineering. The failure of any mechanical system (which is in relative motion) mainly occurs due to wear and friction in terms of material and energy loss respectively (Czichos, 2000). Therefore, the knowledge of tribology helps in improving the service life and safety of the equipment, and considerable economic benefits. The knowledge of tribology helps in reduction of friction and wear in a machine as well as enhance the service life of machinery. In tribology, lubrication has an important role to control both friction and wear. The external substance that applied between the mating surfaces is called the *lubricant*. Thus, any material (either in solid, liquid or gaseous state) having the capability to reduce friction and wear between two dynamic contacting surfaces can be termed as lubricant.

Lubrication was in practice from the ancient time but the development and understanding of the technology triggered between 1750 and 1850 as Industrial revolution (Mang et al., 2010).

Nowadays about 85–90% of the lubricating oil produced from the non-renewable petroleum base stock worldwide (Erhan et al., 2006). However, with diminishing petroleum stock and increasing environmental concern, conventional petroleum resources are restricted in use for many applications. Therefore, once again vegetable based oils are being focused as a renewal source.

1.2. Function of lubricants

The primary purpose of the lubrication is to reduce friction between the mating surfaces. However, efficient and purposeful lubrication means "*Application of correct quality of lubricant in proper quantity at right time*". The critical points of lubrication include the application method, correct quality, proper quantity and the right time.

The objectives of the lubrication categorized as primary and secondary. The primary purposes of lubrication are as follows:

1. *Antiwear and antifriction* – Friction and material loss between dynamic mating surfaces in the presence of lubricant is much less as compared to an absence. It is because the external substance i.e. lubricant alters the interaction of the mating objects from surface-surface to lubricant-surface.
2. *Heat transfer* – All the states of the lubricant is capable to transferring the heat. However, liquid lubricants are more effective due to high specific heat capacity than other states. Generally the lubricants are circulated continuously to and fro inside the system to extract the heat.
3. *Reduction of power requirement* – Lubricant tends to keep the moving parts separate and free run of the contacting surfaces. It reduces the power consumption

along with a reduction in operating noise, and vibrations. It results in a reduction in power cost.

The secondary purposes enlisted as below:

1. *Removal of wear debris* – Lubricants are also helpful in removal of in-situ generated debris and foreign contamination that get introduced into the system.
2. *Extended useful life* – Lubricants increases the useful life of the equipment and its components by decreasing the material loss and rubbing friction.
3. *Minimize breakdown* – Lubricant reduces unscheduled downtime due to breakdowns of potentially costly equipment by avoiding excessive generation of heat, friction, and seizure etc.
4. *Reduction of thermal stresses* – Lubricant also act as a coolant. Since a local heat generated due to rubbing of the surfaces, which produces thermal stress inside the body. Therefore, on the application of the lubricants, it can be avoided.
5. *Sealing from the environment* - Lubricants may be introduced in the clearance between moving parts like piston and shaft and act as sealing agent.
6. *Rust and corrosion prevention* – The lubricants formulated with additives react with the metallic surfaces to prevent corrosion and rust.

1.3.Types of lubricant and additives

There are three types are lubricants used in industrial/commercial applications i.e. solid, semi-solid, and liquid; somewhere air is also used. Solid lubricants are generally in the powders form. Some of the well known powder lubricants are graphite, molybdenum disulphide (MoS_2), tungsten disulphide (WS_2), polytetrafluoroethylene (PTFE) etc. Solid lubricants can work efficiently up to the 350°C which is higher than other class of lubricants.

Semi-solid lubricants (like greases) produced by uniform blending of lubricating oils with various thickening agents. Thickening agents may be soaps, organic or inorganic substances. The solid particulates can also be used in the greases and their consistency closely resembles like paste. Grease can have a range of viscosities and are available generally in semi-solid state, however solid like form is also available known as block greases.

Table 1.1. Classification of lubricant additives.

Additive type	Purpose
Lubricant protective additives	
Antioxidant	To improve oxidation stability of the lubricant
Metal deactivator	Decrease catalytic effect of metals on oxidation rate
Antifoamant	To avoid the continuous foam formation
Surface protective additive	
Rust corrosion inhibitor	To avoid rusting and corrosion of the metallic parts
Anti-wear agent	To reduce material loss and prevent against seizure
Friction modifier	To improve the friction properties
Detergent	To keep the lubricated surfaces contamination free
Dispersant	To keep solid additives or contamination dispersed
Performance additive	
Viscosity improver	To improve viscosity changes with temperature
Pour point depressant	Enhance the flow property of lubricant at low temperatures
Seal swell agent	Cause swelling of elastomers by chemical reaction

Liquid lubricants identified on the basis of their origin like mineral, synthetic and vegetable oil. In general, liquid lubricants are viscous fluids, and it is circulated through the different machine elements by using rotary mechanical systems like bearings or gears. Detailed discussion on the base oils is reported in chapter-2.

A lubricant in pure/raw condition, sometimes, is not capable of performing its intended function. Therefore, a small amount of external substance is added in the lubricant to overcome the particular drawback. The external substance added in the lubricant called as an additive. Additives may be chemical reagents (soluble in oil) or micro- to nano-sized particles that form colloids with the oils. The additives classified according to the specific function as in Table 1.1.

1.4. Nanoparticles as a lubricant additive and its advantage over conventional additives

Lubrication plays a crucial role in stemming the physical or chemical interaction between the mating surfaces as well as after-use environmental impacts. Therefore, additives in the lubricant are mandatory to sustain in the various operating conditions (Dai et al. 2016). There are two primary considerations for any lubricant manufacturer during the development of lubricating oil; first, to fulfill intended performance and second, effect on the environment. This is because various government policies have been made considering environmental issues worldwide. Different types of organic and inorganic additives are being used in the lubricants, but it has specific benefits and limitations. Also, from the last two decades, nanoparticles are getting much attention in the lubricating oil and found comparable or better results than conventional additives like zinc dialkyldithiophosphate (ZDDP) that contains toxic elements. Few key points are presented below about the drawbacks of traditional additives and effect of nano-additive in lubricant:

Disadvantages of conventional additives

- Inferior thermal stability at a higher temperature.
- Mostly contains environmentally hazardous elements like sulfur, phosphorus.
- Increases toxic emission that affects the human being, animals, and environment directly.

Advantage of nanoparticles as lubricant additives

- Potential to reduce toxic emission.
- Improving fuel economy.
- Superior thermal stability at elevated temperatures.
- In tribological contacts nanoparticles (less than 100 nm size) can easily enter in the contact zone, separate the friction surfaces and improves tribological properties.

1.4.1. Role of nanoparticles in lubricant

The nanoparticles have higher surface area per unit volume as compare to the micro-sized particles; therefore it can smoothen and separate the mating surfaces effectively by mending, polishing, rolling phenomena etc (Dai et al. 2016). The major problem with the solid nano-additives is agglomeration. In this regards different dispersants can be used or modify the surface of nanoparticles for uniform suspension in the oil for a longer time. Importantly, different nano-additives (oxide, nitride, rare earth compound, polymer, etc.) behave distinctly with different oils. It indicates the importance of nanoparticle parameters like shape, size, morphology, and concentration in tribological behavior. The detailed lubricant additive evolution and effect of nanoparticle parameters in tribology has been discussed in chapter 2.

1.5. Lubrication regime

According to the degree of separation of the mating surfaces, the lubrication regime is classified as follows (Figure 1.1);

i. ***Boundary lubrication:*** Considerable asperity-asperity contacts take place and mostly occur during initial start-up or shut down of some machines or at severe loading conditions, thus prone to high friction and wear.

ii. ***Mixed lubrication:*** This regime form at low speed and high load and temperature range. It exhibits the combined behavior of hydrodynamic and boundary lubrication.

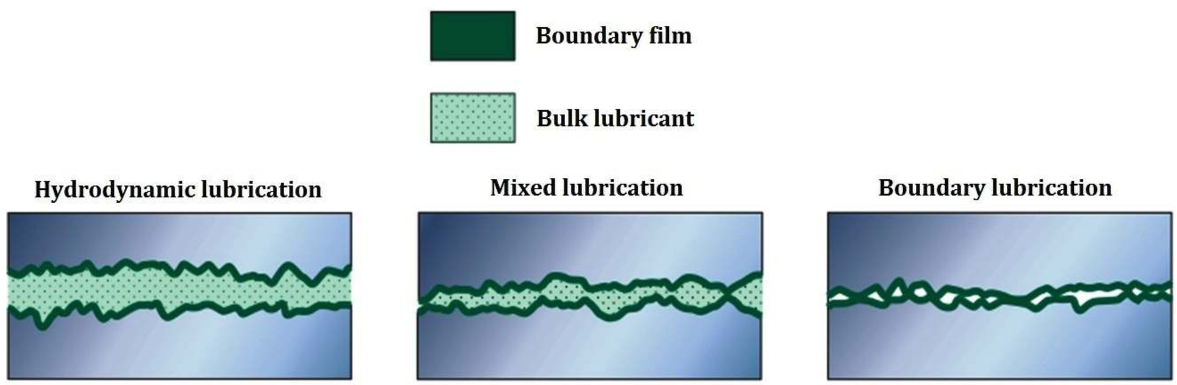

Figure 1.1. Typical image of different lubrication regime.

iii. ***Elastohydrodynamic lubrication (EHL) and Hydrodynamic lubrication:*** In the hydrodynamic lubrication regime, surfaces are entirely separated by the lubricants. This is stable lubrication regime with no metal-metal contact during operation and occurs at high speed and low load. EHL is a subset of the hydrodynamic lubrication in which elastic deformation of mating surface plays a critical role. EHL film thickness is lower than the hydrodynamic lubrication.

1.10. Ongoing lubricant market

Worldwide around 85% of petroleum based lubricants are being used (Pop et al., 2008). Global demand of the lubricant increased from 35 to 35.7 million metric tons from the year

2012 to 2016 and expected to increase by 1.2% in next decade (Figure 1.2). The highest and lowest lubricant demand was in 2006 and 2009 as 36.9 and 32.2 million metric tons respectively. According to OPEC (Organization of the Petroleum Exporting Countries) report 2014, India's and World's oil requirement may increase from 3.7 to 4.6 mb/d (million barrels per day) and 90 to 96 mb/d respectively, considering medium term oil demand for period 2013–2019. However, it may increase from 3.7 to 9.8 mb/d and 90 to 111.1 mb/d for India and world respectively for long term demand during period 2014-2040 (OPEC report, 2014).

1.10.1. International status

About 1700 lubricant manufacturing company from small to large scale exists worldwide. In Europe there are about three hundred manufacturers. About 60% volume of the total lubricants available in the market is produced by 2% of lubricant manufacturers only (Nagendramma and Kaul, 2012). Therefore more than ten thousand lubricants of different categories are available worldwide to use in 90% lubricant applications (Reeves, 2013).

In Europe continent, Germany is most demanding market of lubricants. It consumes about 2.5 million metric tons/year which is about 47% of total demand. However, industrial lubricants consumed is 1.7 million metric tons /year (32%), marine and aviation lubricants consumed is 0.5 million metric tons /year (9.4%) and process oils 0.6 million metric tons/year (11.3%) (Bartz, 1998). Automotive and hydraulic oils are the most demanding group among all industrial oils. In the past 15 years , Europe and the America together lost what Asia-Pacific and rest of world gained, and these last regions now share close to 44% of the global lubricant market (Fuchs, 2000).

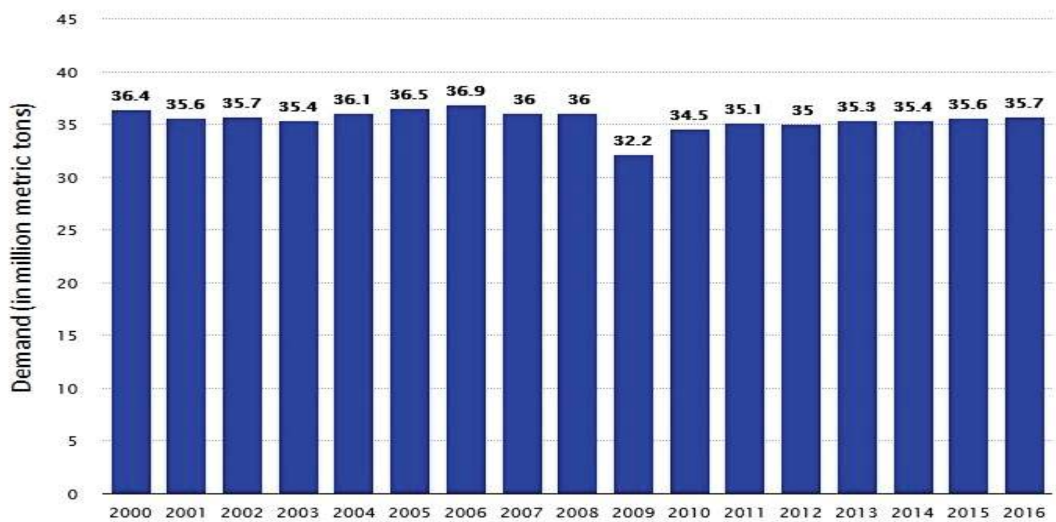

Figure 1.2. Global demand for lubricant from 2000 to 2016.

(Source: www.statista.com/statistics/411616/lubricants-demand-worldwide/)

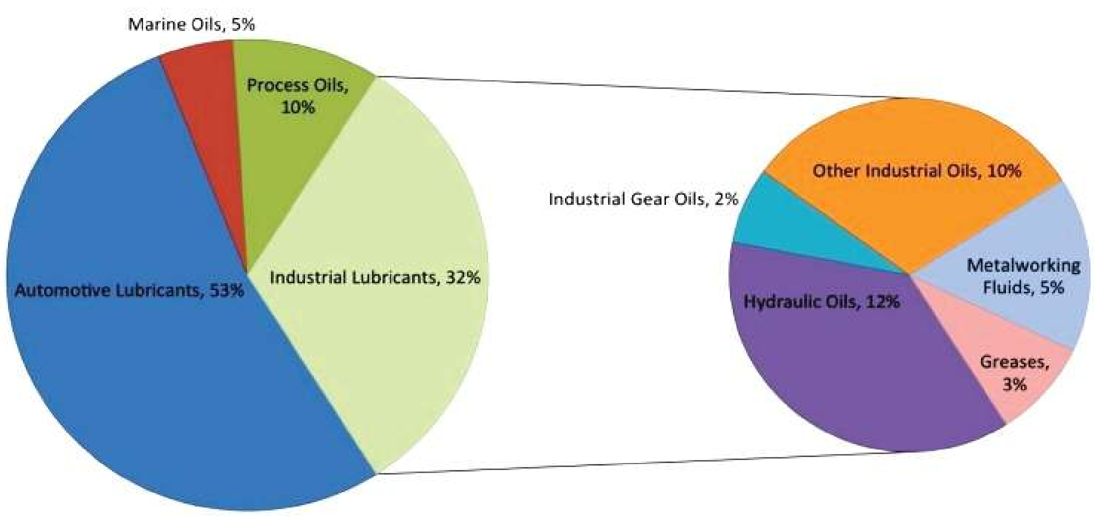

Figure 1.3. Worldwide consumption of the lubricant (Reeves, 2013)

Figure 1.3 shows that industrial and automotive lubricants (combined 85%) are dominating over other lubricant class. Industrial lubricants (about 32%) further categorized to 12% hydraulic oils, 10% other industrial oils (such as bearing oils, refrigeration compressor oil, turbine oils etc), 5% metalworking fluids, 3% greases, and 2% industrial gear oils (Reeves 2013).

1.10.2. Indian status

It expected that hundred million tons petro-product is consumed per year in India. It includes two million tons (approx.) lubricant consumption. The majority of this lubricant consumed in two, three and four wheelers; it makes India distinct from other developed countries. The proportion of these lubricants is 97 and 3% from petroleum and synthetic oils respectively due to the cost consideration (Mobarak et al., 2014). The emission policies considering environment health pressurized the vehicle manufacturer to reduce HC, CO, NOx; so that air quality can improve. In this prospect, non-edible vegetable oils may be the potential substitute.

1.11. Green Tribology

Green tribology categorized into two sub areas, i.e. green engineering and green chemistry. Green Engineering is referred as ‘Development, commercialization and used the approach as well as products must be technically and economically feasible to minimize the pollution and health of the environment and human being. And, Green chemistry is referred to ‘The development of potential chemical products or approaches that must be able to reduce/avoid the use or production of hazardous substances’ (Nosonovsky and Bhusan, 2010).

A typical tribo-system consists of different tribo-pairs in contact, which transforms material and energy by interaction. In case of green tribology following characteristics should be considered; (i) higher wear-resistant materials, (ii) extended service and shelf life of the lubricants, (iii) biodegradable lubricants and (iv) environment adapted lubricants (EALs) having no negative impact on the eco-system. All these characteristics have direct and/or indirect impact on the life cycle assessment (LCA) of any tribo-system working on Green Tribology principle (Anand et al., 2017).

1.12. Importance of Green Lubrication

Green lubricants are the substance obtained from the natural and renewable sources as well as environmentally benign. Green lubrication contributes to energy conservation, reduction of waste and produce potential products. In actual significance the green lubricants are those that optimize the energy efficiency, perform its intended function in the machinery (i.e., reduce friction and wear), maximize the service life without affecting the eco-system.

1.12.1. Reasons to move towards Green Lubricant over petroleum/synthetic oil

1.12.1.1. Continuous increasing lubricant demand

Worldwide the demand of the lubricant is increasing day by day in various industrial and commercial applications, but the petroleum reserves are limited which will be finished in next few years. Therefore for the survival of the next generation, an alternative to petroleum stock is mandatory which can be obtained from the renewable and sustainable sources. In this prospect, the vegetable/animal oil is best suited.

1.12.1.2. *Impact of petro-products from extraction point to dump*

A considerable fraction of lubricant dispersed into the environment either during production (in the form of spill or leaks), during application (in the form of emission of partial combustion and their derivatives loss), or during dumping. It contaminates the soil, air, surface, and groundwater directly (Abdalla and Patel, 2006). The lubricant spilling is also one of the leading problems. A huge amount (approx. 600000 tones) of lubricant lost in the environment per year (Aranzabe et al., 1994). Since lubricants have a lower density than water, therefore it spread over water rapidly. Only 1 liter of lubricant is capable to form oil film of 4000 m^2 over the water (Aranzabe et al., 1994). These are non-degradable therefore damaging effects are left on the aquatic life.

1.12.1.3. Human health and environment

Toxicity and non-degradability of the petro-product are two of the critical parameters for assessment of adverse effect on health of human being, animals, and plants. The used lubricants contain significant amounts of polycyclic aromatic hydrocarbons that are considered as carcinogens for human being (Wong and Wang, 2001). Even after the use, lubricants are very toxic and hazardous to the embryos and newborn animals. Also, the aquatic organisms are adversely affected by the water-soluble proportion of lubricants (Hedtke and Puglisi, 1980). Plants are also vulnerable because the used lubricants deteriorate the soil property and reduce the fertility. Sea water and underground water reserve are even started to infect day by day due to; (i) dumping of the used lubricants in rivers, (ii) spillage of lubricants and entering to water source by storm water runoff (Hedtke and Puglisi, 1980). These petro-products do not degrade with the passing of time, thus adversely impact on ecosystem health throughout its lifespan.

1.12.1.4. Green lubricants: Superior in boundary lubrication

Green lubricants i.e. biolubricants are polar in nature; therefore possess more active sites (carboxyl acid or esters) to interact with the dynamic mating surfaces. These lubricants also have strong bonding and adhesive interaction (Hsien WLY, 2015). Thus, at par or better performance can be achieved by biolubricants in boundary lubrication regime than mineral and synthetic oils.

1.13. Summary of the chapter

This chapter gives deep insight about the demand, availability and environmental effect of different lubricants. Considering the above points, the present work motivates to move towards green lubrication for different tribological contact situations.