ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ALTERNATIVES FOR FOUR STROKE MOTORCYCLE ENGINE OILS

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ABBREVIATIONS AND ACRONYMS

API	: American Petroleum Institute
ASTM	: American Society and Testing Materials
B.C.	: Before Christ
°C	: Celsius
CCS	: Cold Cracking Simulation
CEC-L	: Coordination European Council
cSt	: centiStoke
DIN	: Deutsches Institut für Normung
EU	: European Union
EVA	: Ethylene Vinyl Acetate
F_f	: Friction Force
g	: Gram
ISO VG	: International Standards Organization Viscosity Grade
KOH	: Potassium Hidroxide
ME	: Canola Methyl Ester
MO	: Mineral Oil Motor Oil
MOME	: Mineral Oil Methyl Ester
MSC	: Malan Styrene Copolymer
N	: Newton
POAS	: Petrol Ofisi Anonim Sirketi
OCP	: Olefin Copolymer
OPEC	: Organization of Petroleum Exporting Countries
PAO	: Polyalphaolefin
PIB	: Polyisobutylene
PMA	: Polymethacrylate
Rpm	: Round Per Minute
SBR	: Hydrogenated Butadiene
SIP	: Hydrogenated Styrene-isoprene Copolymer
SO	: Synthetic Oil Based Motor Oil
SOME	: Synthetic Oil Methyl Ester Based Motor Oil
VI	: Viscosity Index
μ	: Friction Coefficient

ALTERNATIVES FOR FOUR STROKE MOTORCYCLE ENGINE OILS

SUMMARY

For centuries lubricants are used for reducing friction between moving two surfaces. In the early age's water, vegetable oil and fat is used, then with the growth of the petroleum refinery, mineral oils are started to be primary base oil for the lubricant market. At the industrial revolution and World Wars to fit the markets requests, synthetic based lubricants are used and become the main product of the lubricant market for years. Today, mineral and synthetic based lubricants are widely used. But for the reason of ecological aspects, which are gaining importance in nowadays and limited resources of mineral oils, environmentally friendly biobased lubricants are gaining importance. Biobased lubricants are also important for using national resources rather than importing crude oils which are limited. The main consumption of lubricant market is motor oils. In our study, starting from mineral, synthetic and biobased lubricants; mineral, synthetic, biomineral and biosynthetic based four stroke motorcycle engine oils (10w40) are prepared, then lubricant and lubricity properties of the motor oils are determined. The results show that 5% of biobased lubricants will be suitable for preparing 10w40 motor oils in both mineral and synthetic based motor oils. Also improvements in the lubricity properties with the blend with biobased lubricants are seen. Biomineral and biosynthetic 10w40 motor oils become alternatives as motorcycle motor oils.

DÖRT ZAMANLI MOTORSİKLET MOTOR YAĞLARI İÇİN ALTERNATİFLER

ÖZET

İlk çağlardan günümüze, hareketli iki yüzey arasında sürtünmeyi azaltmak amacıyla yağlama yağları kullanılmaktadır. İlk dönemlerde kullanılan yağlama yağları su, hayvansal veya bitkisel kökenli iken, petrol rafinasyonunun hızla gelişimi ile mineral yağların yağlama yağları olarak kullanımı artmış, endüstri devrimi ve İkinci Dünya Savaşı'nın ardından, artan endüstriyel ihtiyacını karşılayabilmek amacı ile, sentetik esaslı yağlama yağları kullanılmaya başlanmıştır. Günümüzde yağlama yağları mineral ve sentetik yağlar olarak pazarda mevcuttur. Fakat artan küresel çevre sorunları, tüm uygulamalarda olduğu gibi, yağlama yağları sektörünü çevre dostu yağlar üretmek konusunda zorlamaktadır. Ayrıca ham petrol ithalatı yerine doğal kaynak kullanımı biyobazlı yağlama yağlarının önemini arttırmıştır. Yağlama yağı sektöründe motor yağları en büyük paya sahiptir. Bu çalışmada, mineral, sentetik ve biyobazlı yağlama yağlarından başlayarak; mineral, sentetik, biyomineral ve biyosentetik 10w40 motorsiklet motor yağları üretilmiş, yağlama yağı özellikleri ve yağlayıcılık özellikleri belirlenmiştir. Sonuçlar %5 oranında biyobazlı yağlama yağlarının, mineral ve sentetik bazlı 10w40 motorsiklet motor yağlarında kullanımının mümkün olduğunu göstermiştir. Ayrıca, biyobazlı yağlama yağlarının harmanlanmasıyla birlikte, yağların yağlayıcılık özelliklerinde de artış gözlenmiştir. Biyomineral ve biyosentetik 10w40 yağlar, motorsiklet motor yağları için alternatif olarak önerilmiştir.

1. INTRODUCTION

Lubricants are used to reduce friction and wear between two moving parts. Besides their primary functions they are also used in heat transfer, contaminant suspension, liquid sealing and corrosion protection.

First lubricants are derived from animal fats and till that time lubrication is done by using biobased oils and fats. But, as the discovery of mineral oils which can be refined to produce high quality and easily producible lubricants, mineral oils become predominated.

For today, lubricants are mainly derived from petroleum oils and synthetic esters, because of their low production costs and low biodegradability. But mineral based and synthetic ester lubricants will not be enough to reach the future requirements. Because future lubricants require low toxicity especially when exposed to environment, low coefficient of friction, better load carrying ability, low evaporation rate. New lubrication researches began to produce the future lubricants.

The results may be available in the biodegradable and harvestable raw material based biolubricants. Especially for the environmental aspect and good performance abilities, biobased lubricants may become the primary solution for the future.

In this study, starting from mineral, synthetic and biobased lubricants and mineral, synthetic, biomineral and biosynthetic four stroke motorcycle engine oils are prepared, lubricant and lubricity properties are tested and candidate of lubricating oils are presented.

2. THEORETICAL PART

In this part of the study, theoretical study results will be presented on following subjects, respectively:

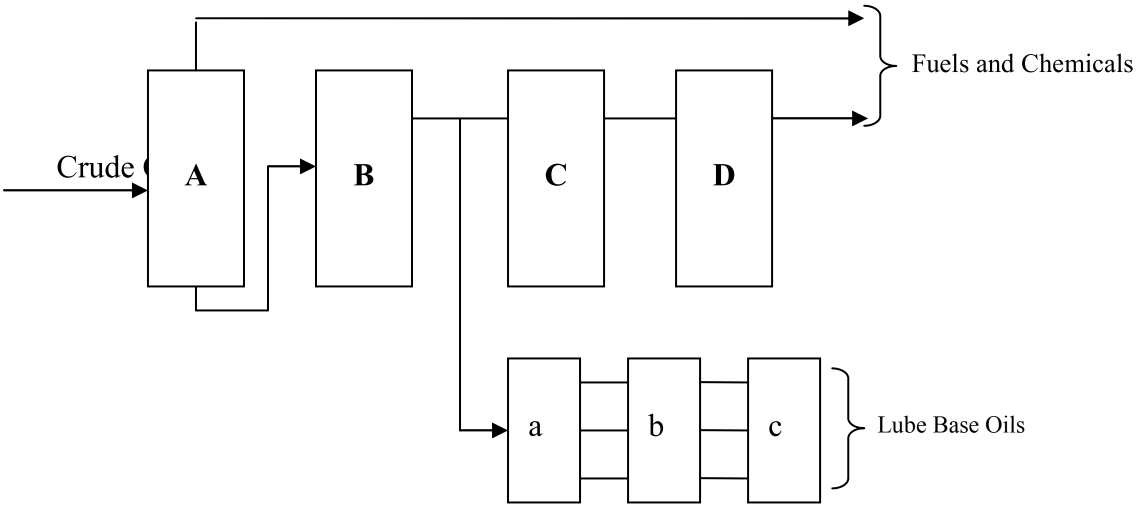
- Mineral Oils
- Synthetic Oils
- Oil Additives
- The Overview of Lubricant Market
- Environmentally Friendly Lubricants
- Engine Oils
- Literature Review

2.1 Mineral Oils

Base oils are the most important parts of the lubricants. Normally more than 95% of lubricants average weight is base oils. These values increase in some families of lubricants (e.g. hydraulic and compressors oils) up to 99% and with only 1% of additive [1].

Mineral base oils are the distillation product of crude petroleum oils. The crude oils is consists of thousands of single components so they also reflected to the distillation fractions. That is why mineral oils are defined as technical properties of mineral base oils. Normally mineral base oils are defined as boiling rage of 200^0C-550^0C crude oils but specialized grouping techniques are also available [2].

The process of converting crude oil into finished base oil is done generally with refining processes. As far as base oil manufacturing is concerned, the actual refining process begins after the distillation stages. In Figure 2.1 the block diagram of the refining process for lube base oil is shown. In Figure 2.2 the distillation curve for crude oil is shown. The distillation of lube base stock can be seen between 370°C to 480°C.



A	: Atmospheric distillation
B	: Vacuum distillation
C, D	: Processing of vacuum distillates for non-lube production
a,	: Fractionating vacuum distillation
b, c	: Lube refining processes

Figure 2.1: Block Diagram of Refining of Lube Base Oil from Crude Oil Process [2].

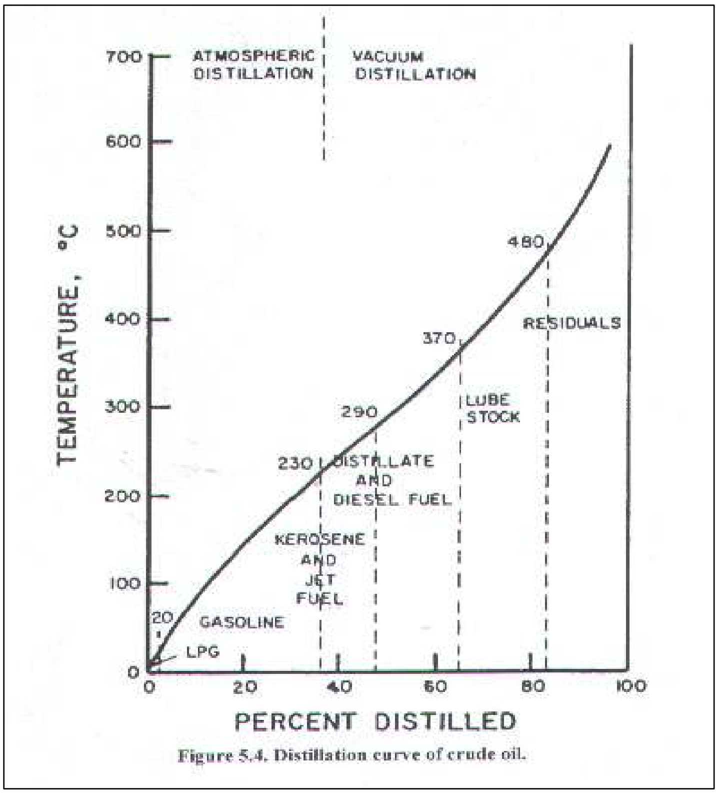


Figure 2.2: Distillation Curve of Crude Oil [1].

Crude oils which yield high-grade base oils are preferred for the production of lube base oils. Of importance to vacuum gas oils which are derived from the crude oil and which are the direct feed for lube refining are particularly, viscosity index, wax content and sulfur content. The finished base oils have high sulfur content, especially after conventional solvent refining. Hydrogenating processes almost fully eliminate sulfur but desulphurization consumes hydrogen. In Table 2.1, some properties of mineral oil are given. After the lube base oil produced, additives have to be added to improve properties required in the usage area.

Table 2.1: Properties of Mineral Oils [3].

Properties	Base Oil			
	Spindle	Light Neutral	Heavy Neutral	Bright Stock
Viscosity, 100°C, cSt	3.3-4.0	5.2-5.7	10.8-11.6	33-36
Viscosity Index	95	100	95	90
Total Acid Number, mgKOH/g	0.1	0.1	0.1	0.1
Flash Point, °C	180	220	246	292

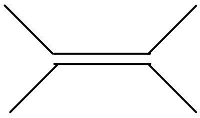
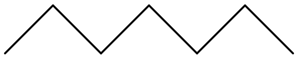
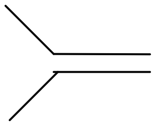
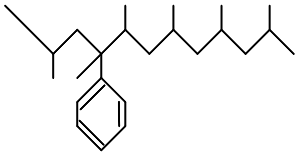
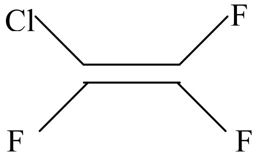
2.2 Synthetic Oils

By the improvement of the industry, the lubricants are required to be highly performed, high and cold temperature stable fluids. But the simple mineral or vegetable oils can’t achieve these requirements without having any modification. The chemically modified lubricants are called synthetic lubricants.

There are always been three reason for development of new synthetic lubricating oils. The first is to achieve a lower temperature-dependence of the physical properties, for example, to make either higher or lower temperatures accessible; the second is to obtain better inertness, for example to prolong the performance time.

In Table 2.2, the synthetic oil groups are given. The synthetic esters which are an important group of synthetics oils are described in section 2.2.1.

Table2.2: The Classes of Synthetic Oils [2].

Synthetic Lubricant Group	Example Formula of a Lubricant	Example
Synthetic Hydrocarbons		Polyethylene derivatives
Polyalphaolefins		Monomer
Polybutenes		Isobutene
Alkylated Aromatics		Alkyl benzene
Halogenated Hydrocarbons		Chlorotrifluoroethylene

2.2.1 Synthetic esters

Synthetic dibasic and polyol esters were developed for commercial use during World War II to satisfy the demands of aircraft engine oil and have many outstanding performance characteristics. Natural oils, mostly animal fats, have been used since 1400 B.C. The rise of synthetic lubricating oils on an industrial scale began in 1931, when Sullivan published the results of their attempts to make tailor-made saturated lubricating oils with low pour points by catalytic polymerization of olefins. In Table 2.3, the groups of synthetic esters are given [2, 4].

Table2.3: Classes of Synthetic Ester Type Lubricants [2].

Esters of Carboxylic Acids	
	Dicarboxylic Esters
	Polyol Esters
	Flurinated Carboxylic Acid Esters
Polyethers	
	Perfluorinated Polyethers
Dibasic acid esters	
Fluoro esters	
Neopentyl poly esters	
	Perfluoroalkylpolyethers
Phosphate esters	
	Phosphate esters
	Phosphazenes
Polyglycols	
	Polyalkylene glycols
Polyphenyl Ethers	
	Silahydrocarbons
Silicate Esters	
Siloxanes	
	Polysiloxanes

Below -75^{o}C the performance of commercial dicarboxylic acid esters and siloxane oils ends and only some branched hydrocarbons (for example, 3.3-dimethylhexane) seems to have suitable properties (melting point <125 ^{o}C). Above 300 ^{o}C the pratical performance of commercial perfluorinated polyethers ends. Above 400 ^{o}C the performance of perfluorinated polyethers ends [2].

For today, most of the used lubricants especially for motor oils are mainly synthetic ester type lubricants. New generation esters are researched which has better performances, but real economic values can only be gained, by the proof of the ester in the usage areas [2].

2.3 Oil Additives

Base oil properties are not suitable as a lubricant for the usage areas especially for high performance required areas. The properties have to be improved to satisfy the requirements.

For this reason numerous additives are available to make the mineral oil to suit for the usage area. Lubricant additives are synthetic chemical substances that improved the oils. In market suitable lubricants are available for mineral oils, synthetic oils and also for biobased lubricants.

The types of oil additives are explain below:

- Oxidation Inhibitors
- Viscosity Index Modifiers
- Pour Point Depressants
- Detergent and Dispersants
- Extreme Pressure and Anti-wear Additives

2.3.1 Oxidation inhibitors

The lifetime of a lubricant varies by the oxidation time. The oxidation process of mineral oil can be described by free radical mechanism via alkyl and peroxy radicals are shown below [2].

Initiation:

$RH \xrightarrow{+O_2} R\bullet$

Chain Propagation:

$R\bullet + O_2 \longrightarrow ROO\bullet$

$ROO\bullet + RH \longrightarrow ROOH + R\bullet$

Chain Branching:

$ROOH \longrightarrow RO\bullet + \bullet OH$

$RO\bullet + RH \longrightarrow ROH + R\bullet$

$\bullet OH + RH \longrightarrow H_2O + R\bullet$

Termination:

$2\,R\bullet \longrightarrow R - R$

To prevent this reaction synthetic additives which holds free radicals are used. This radicals are mainly Zinc dialkyl dithiophosphates, compounds of nitrogen and sulfur, hindered phenols and Bis-phenols [1].

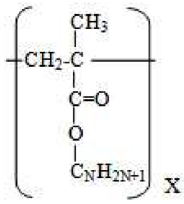
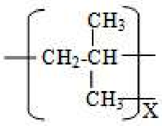
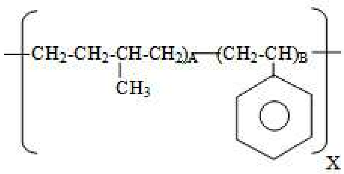
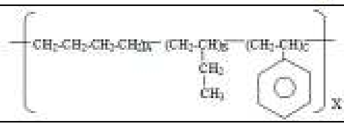
2.3.2 Viscosity index modifiers

In high performance lubricating systems viscosity is one of the main properties which classify the lubricant as suitable for the usage systems. In the lubricating systems the viscosity index has to be between the defined range. To modify the base oil viscosity to the required viscosity range some specialized mainly polymer based viscosity modifiers are used.

Viscosity index of a lubricant depends on the molecular weight and the concentration. In practice depending on the projected application, molecular weights of 10,000 to 250,000 g/mol of chemicals are used. Concentrations are used between 3 to 25% (w/w). This makes the viscosity index modifiers are mainly the additive for lubricants [2].

Apart from the fundamental description of thickening effect and shear stability, the expert differentiates viscosity modifiers by the molecular structure, composition and chemical nature of the individual chain links (monomer). In the Table 2.4 mainly viscosity modifier groups are listed below.

Table2.4: Types of Polymeric Viscosity Modifiers [2].

Description	Formulation	Main Applications
Olefin Copolymers: OCP		Engine and Hydraulic Oils
Polyalkyl(methyl)acrylates: PAMA		Gear and Hydraulic Oils
Polyisobutylene: PIB		Gear oils, Raw Material for Ashless Dispersants
Hydrogenated styrene-isoprene copolymers: SIP		Engine Oils
Hydrogenated styrene-butadiene: SBR		Engine Oils

2.3.3 Pour point depressants

The lubricants have to work on cold conditions in some applications. For this reason lubricants have to be able to flow on cold temperature conditions. To improve the cold flow of base oils pour point depressants are used. Pour point depressants are like with viscosity index improvers. They effect on the easily crystal able paraffinic based compound and crack the crystallization product. Normally they are added about 0.1% to max 2% (w/w) to the lubricant. Some of the formulations of the lubricants are below. In Figure 2.3 general pour point depressant types are shown [5].

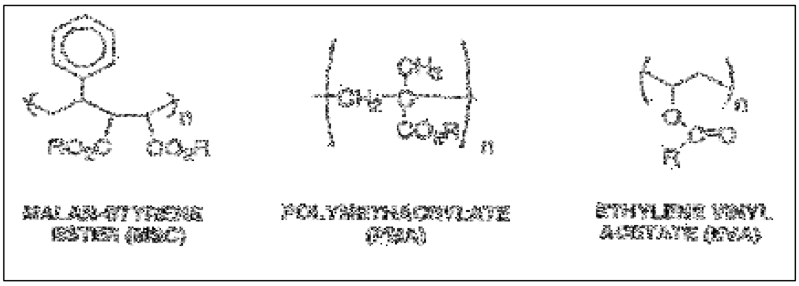


Figure 2.3: Types of Pour Point Depressants [5].

2.3.4 Detergents and dispersants

Detergents and Dispersants are heavy duty additives which work on stressed applications and keep the lubricants insoluble from the consumption products and also asphalt like oxidative solid particles. These additives mainly have a large oleophilic hydrocarbon "tail" and a polar hydrophilic head group. The tail section serves as a solubilizer in the base oil, while the polar group is attracted to contaminants in the lubricant In Figure 2.4, dispersant function is shown. These additives can be mainly phenate, saliclate, thiophosphonate, sulfonate, amine compounds [1].

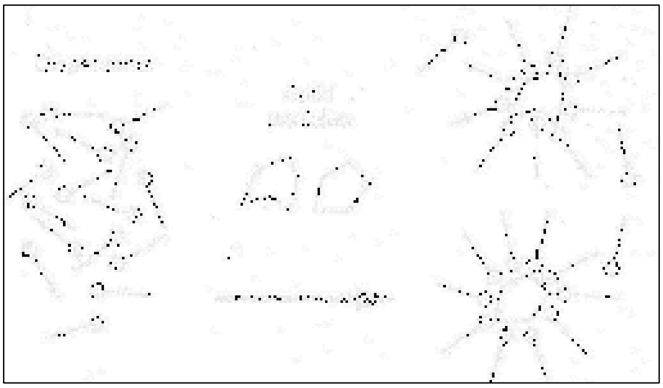


Figure2.4: Function of Dispersant Process [2].

2.3.5 Extreme pressure and anti-wear additives

When two contacting part start to move and the hydrodynamic lubrication has not built up or in the case of severe stress and strong forces the lubricating systems run in the area of mixed friction. These additives form a protective film surface and reduce wear and prevent sizing. These additives are mainly, phosphorus, sulfur, nitrogen, chlorine compounds [2].

2.4 The Overview of Lubricant Market

The overview of the lubricant market is explained below:

- World Lubricant Market
- Turkey Lubricant Market

2.4.1 The overview of lubricant market in The World

The crude oil is the resource of mineral oil and this makes the crude oil to be the main resource of lubricant. The reserve of the lubricant market

The biggest reserve of the World is located in Middle East Asian countries with 185.9 billion m^3 reserve and require to have and growth rate of %34 until 2025.

At the same time OPEC (organization of the petroleum exporting countries) also require from members to increase the production rates 1.5% until 2030. Even with the increase in the production of OPEC member companies and the reserve growth rates, the requirement of oil in all over the World increases. These can be seen from the price increase rates of m^3 in all over the World. The price of the m^3 s was 84 US$/ m^3 in 1994 and the best estimation of the oil prices will foreseen to be 208 US$/ m^3 in 2030. These values will increase if any crisis for oil occurs [6].

Table 2.5: Estimated World Oil Resources 1995-2025(Million Tons) [7].

Oil Resources	OPEC	Non-OPEC	Total World
Proved Reserves	901.7	390.9	1292.5
Reserve Growth	395.6	334.6	730.2
Undiscovered	400.5	538.4	938.9
Total	1697.8	1263.9	2961.6

As it is seen, the crude oil resources are limited in the World so this makes the renewable resources for lubricants will gain importance in the future.

World's lubricant consumption statistics are not available, only limited data is available for European consumptions. Totally 5.3 million tons/year lubricant is consumed in Europe (see Figure 2.5). In Germany, 1.15 million tons/year lubricant is sold. 53% of these amounts are collected as waste oils. These are then recycled or used as a source of heating fuel. The rest, about 540 thousand tons is lost to the environment as a result of leakages, evaporation or total loss applications (metalworking fluids, chainsaw lubricants etc.). These losses cause pollution to the environment. The European Union (EU) member's total consumption of lubricants is shown in Figure 2.5 [8, 9].

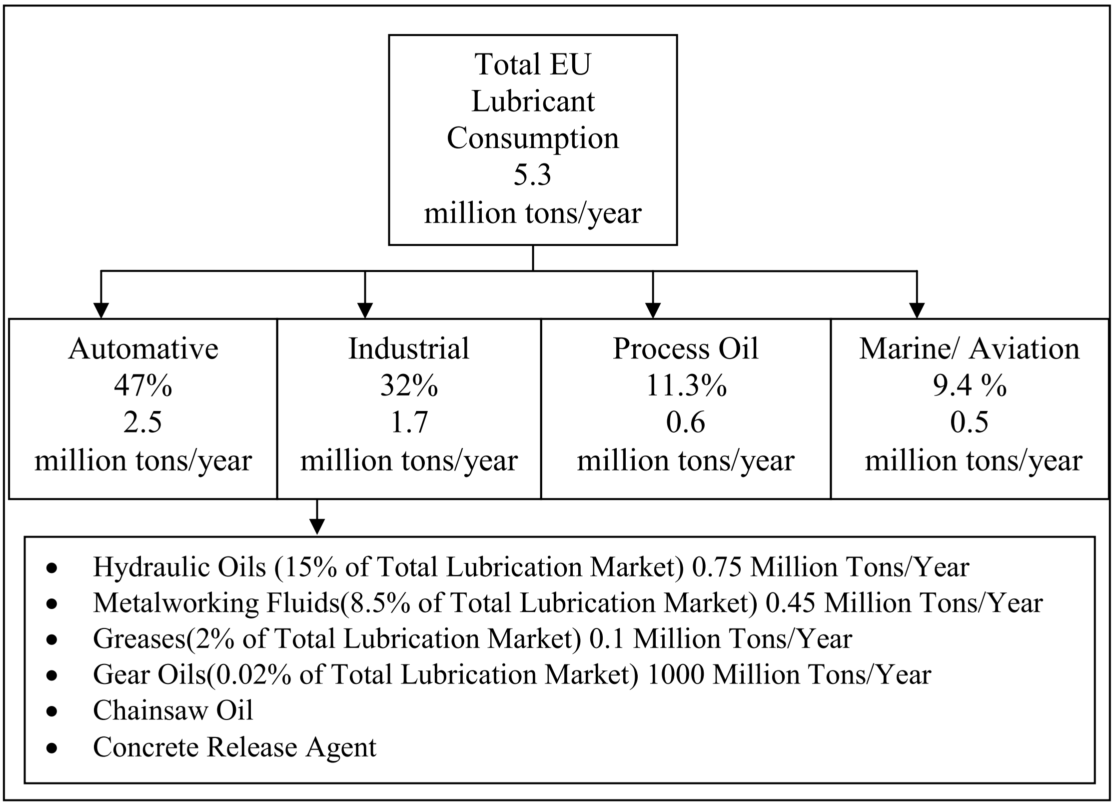


Figure 2.5: European Union members Total Lubricant Consumption per Year (2005) [9].

2.4.2 The overview of lubricant market in Turkey

There are no statistics for Turkey lubricant sales. There is limited data available for Petroleum Industry Association (PETDER) registered companies. In Figure 2.6, 2.7, 2.8, the consumption in Turkey from PETDER registered companies is shown. The figures show that, in year 2000 the main consumption in Turkey was 315.048 thousand tons and this value increase to 341.227 thousand tons in year 2005. This makes 7.7% of increase just in 5 years. Also you can see in Figure 2.6 that the main consumption is on motor oils.

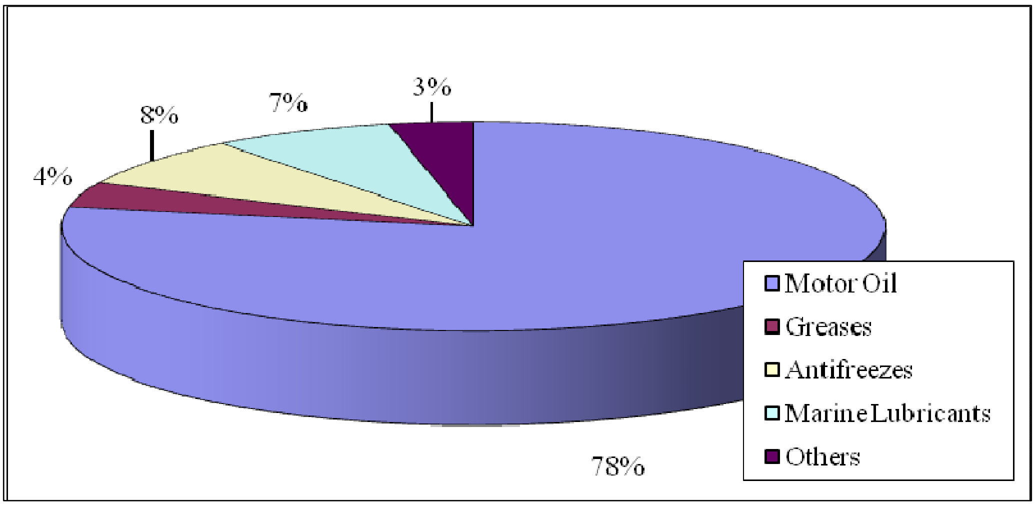


Figure 2.6: Sales of Lubricants by types from PETDER registered companies [10].

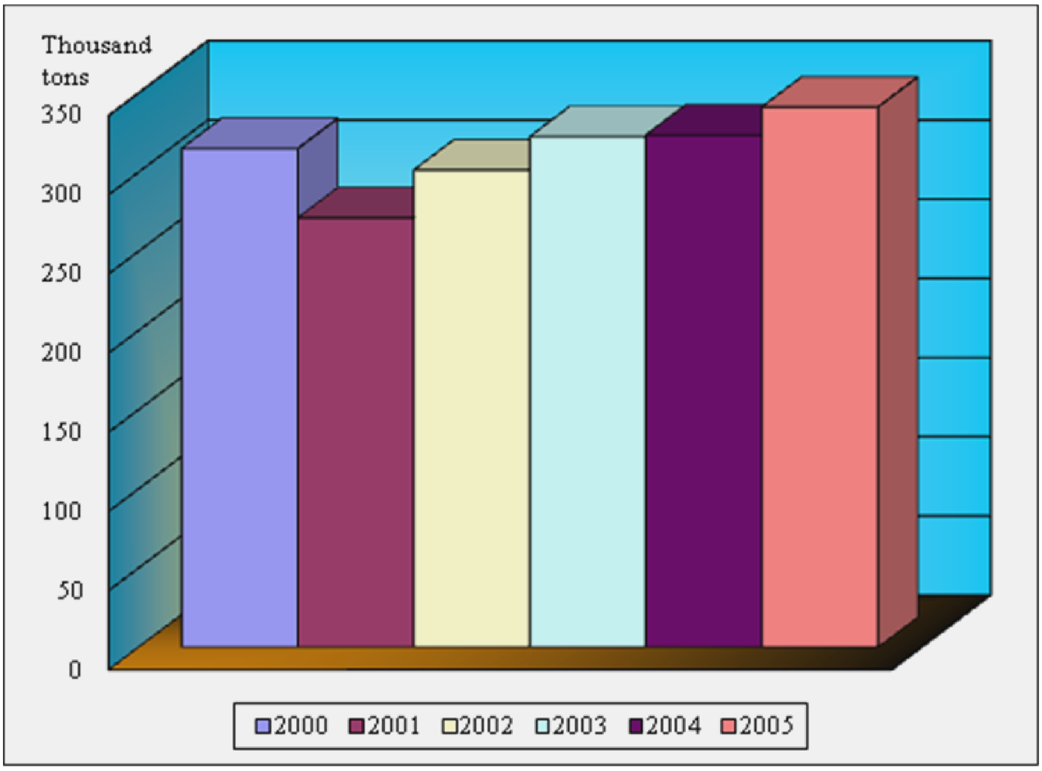


Figure 2.7: Total Lubricant Consumption in Turkey By PETDER Registered Companies [10].

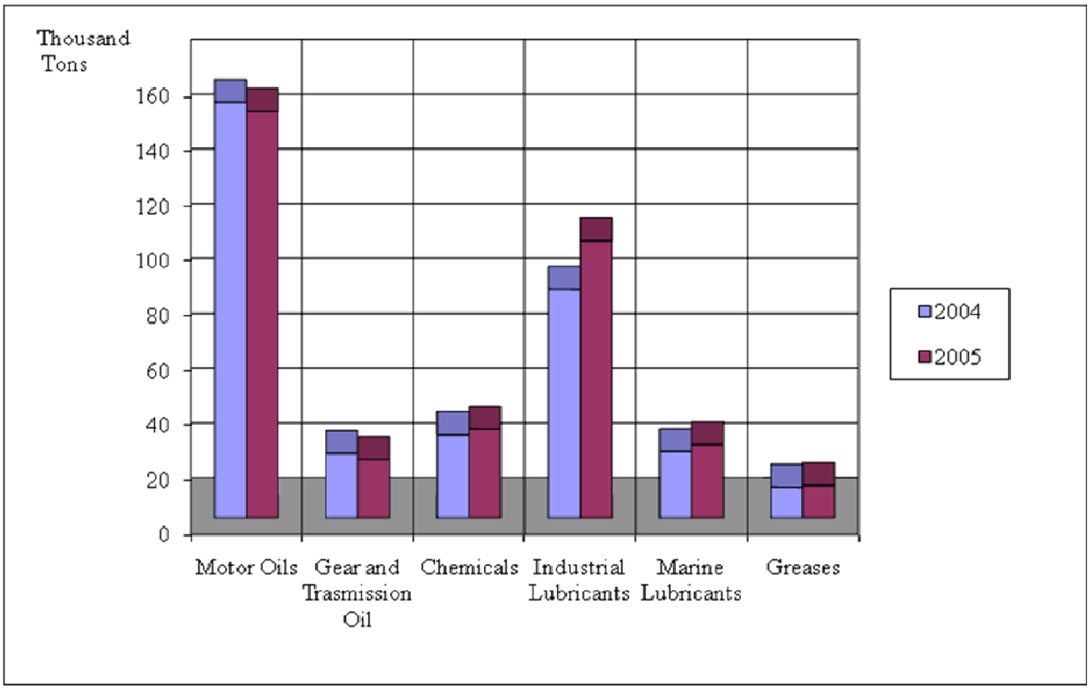


Figure 2.8: The Change in the Lubricant Purchase of 2004-2005 From PETDER Registered Companies [10].

2.5 Biobased Lubricants

Ecological aspects are gaining importance. Our environment is being increasingly contaminated with all kinds of pollutants; any solution for reduction is required. A large proportion of lubricants pollute the environment either during usage or after use. This is for the reason of total-loss lubrication, leaks, emissions, spillages or other problems. As far as the environment is concern to produce the future lubrication, researches are focused on to make more stable high performance environmentally acceptable lubricants.

Environmentally acceptable lubricants are classified in three categories [10].

- **Tertiary lubricants:** The lubricants that are produced from recycled components are called tertiary lubricants. Motor oil made with re-refined base stocks have been used since1992 by Renton Maintenance Facility, Motor Pool and Solid Waste Facility in King County Seattle, Washington. Also re-refined motor oil is used by 1200 buses in the same nation [11].

- **Secondary lubricants:** The lubricants to help to minimize the pollution generated by machines are called secondary lubricants. Energy-conversing motor oils, emission-friendly diesel oils are in this type of lubricants [12].

- **Primary Lubricants:** The lubricants that are non-toxic biodegradable when exposed to environment, high performance lubricants are called primary lubricants.

Lubrication in the future can only be done with environmentally friendly ones. But to be environmentally friendly won't be enough for a lubricant to be selected as future lubricant.

New generation lubricants required to match the future requirements of the market.

Next generation lubricant needs some properties:

- The lubricant must be capable of maintaining an efficient lubricating film between all pairs of working surfaces in the engine under operating conditions.
- The lubricant must be chemically stable, anti-corrosive, and show good chemical resistance to oxidation in the working environment and through the temperature range over which the engine will operate.
- The lubricant should have a high viscosity index, combining easy starts and low oil shearing losses with adequate viscosity at maximum running temperature.
- The lubricant should preferably have detergent properties capable of inhibiting deposit formation in the engine over the range of operating conditions.
- The lubricant must have film strength adequate for bearing surfaces that have very high loadings.
- For the lubrication of some two-stroke engines, the oil must be miscible with gasoline. (Vegetable oil in lubricants and Additives stated for strong growth)

In the primary studies none of properties of the vegetable oils have been reached all of the above requirements [13].

The environmental aspects and the limited sources of crude oil will make biobased lubricants available in the future market. Biobased lubricants have some advantages and also on the other hand have some limitations also.

By having biodegradability property, good antiwear property renewable resources bio based lubricants are going to be the major lubricants available on market. But on the other hand some performance limitation has to be improved. These limitations are poor oxidative stability, deposit formation tendency, low temperature solidification, low hydrolytic stability and narrow viscosity range availability.

By having some additives some of the properties can be improved to produce more efficient lubricants. These properties are lubricity antiwear protection, load carrying capacity, rust prevention, foaming, demulsibility.

In Table 2.6, the properties of lubricants and the vegetable oils are shown and the viscosity, viscosity index and pour point tests are done according to American Society and Testing Materials (ASTM) methods D445, D2270, D97 respectively. The NOACK volatility test result is done according to Deutsches Institut für Normung (DIN) methods in DIN 51581, and biodegradability test method is done according to Coordinating European Council test methods in CEC-L-33-T-82. In the table biodegradability of vegetable oils can be seen as 75-100%, but on the other hand other lubricants vary from the chemical composition and can have biodegradability down to 7%. This leads to deposit formation and pollutes the environment after use.

Biobased lubricants are described below:

- History of biobased lubricants
- Limitations and current solutions for biobased lubricants
- Biobased lubricant market
- Usage of biobased lubricants.

Table 2.6: Properties of Various Lubricant Fluids [2].

	Viscosity, cSt		Viscosity	Pour	NOACK	Biodegradability
	100°C	40°C	Index	Point, °C	Loss,%	%
Polyalphaolefin						
PAO 2	1.8	5.54	-	-65	99	75-92
PAO 4	3.9	16.8	129	-70	12	52-72
PAO 6	5.9	31	138	-68	7	20-23
PAO 8	7.8	45.8	140	-63	3	20-22
PAO 10	9.6	62.9	134	-53	2	16-21
PAO 40	40.0	395	151	-34	0.8	-
PAO 100	100.0	1250	168	-20	0.6	-
PAO 2.5	2.4	8.3	-	-42	-	-
PAO 5	5.0	24.2	145	-50	5.5	-
PAO 7	7.0	38.4	145	-43	2.3	-
PAO 9	9.0	55.9	143	-42	1.5	-
Synthetic Esters						
Diesters						
2 Ethylhexyl						
Adipate	2.4	8	124	-68	44.3	97
Azelate	3.0	10.7	137	-64	29	99
Sebacate	3.1	11.8	126	-60	18.3	96
Dodecanedioate	3.8	14.3	168	-57	-	-
Isodecyl						
Adipate	3.6	15.2	121	-62	15.5	84
Azelate	4.3	18.1	151	-65	9.8	86
Sebacate	4.8	20.2	169	-60	6.2	100
Dodecanedioate	5.2	23.4	162	-41	4.3	93
Isotridecyl						
Adipate	5.4	27	139	-51	4.8	92
Sebacate	6.7	36.7	141	-52	3.7	80
Dodecanedioate	7.6	40.7	156	-50	2.9	76
Polyols						
Trimethylolpropane						
n-heptyl	3.4	13.9	120	-60	11.8	100
n-nonyl	4.6	21	139	-51	2.3	100
Oleate	9.4	46.8	191	-39	-	100
iso-nonyl	7.2	51.7	98	-32	6.7	7
Neopentylglycol						
n-heptyl	1.9	5.6	-	-64	-	100
n-nonyl	2.6	8.6	145	-55	31.2	97
Pentaerythritol						
n-heptyl	6.1	32.2	140	-7	0.9	100
n-nonyl	11.6	129.2	70	-22	-	8
Vegetable oils						
Soybean	7.6	31	227	-9	-	75-100
Sunflower	7.7	31.6	226	-	-	75-100
Corn	7.7	31.9	223	-15	-	75-100
Castor	19.5	255.5	87	-33	-	75-100
Peanut	8.3	36.9	212	3	-	75-100
Rapeseed	9.1	40.3	217	-18	-	75-100
Olive	8.4	38.3	203	-9	-	75-100

2.5.1 History of biobased lubricants

After wheel was invented, it was discovered that smear of cooked animal fat on the axle made pushing a whole lot easier. But which was better, roast deer fat or boiled pig? Tests were run. Lubrication technology was born. Natural oils, mostly animal fats have been used since 1400 B.C. The main purpose of using lubrication is to separate with a film of some material that can be sheared without causing any damage [1, 14, 15].

In Early stages in Sumerian and Egyptian civilizations lubrication is used in potter’s wheel bearing and it is known that even there were number of sites between the Nile and Tigris where crude oil came to the surface vegetable and animal origin oil is used for lubrication [16].

Before the first car was borned when steam powered engines were available, vegetable oil product engine oils are used as lubricants. With the use of internal combustion engines petroleum fuel become popular and a by product a heavier component of refining became available for lubrication [17].

In the World War I and World War II by the reason of insufficient resources and embargo, petroleum refined lubricants become popular because of the reason of easily producibliity. For over a century, lubricants derived primarily from mineral oils or petroleum distillates have been used to lubricate internal combustion engines.

But for the reason of toxicity, low biodegradability and limited resources mineral oils must be replaces with more eco friendly and more available lubricants. The answer of the question of the future lubricant is valid in the history.

In 1960’s a green revolution occurs and biobased products such as lubricants become popular.

Environmentally adapted lubricants were re-developed in the late 1970’s for outboard two-stroke application in Bodensee, on the border between Germany and Switzerland. The first goal is to change the lubricants to more environmentally friendly ones where it is used in nature. For this reason in the early 1980s in Germany hydraulic fluids are used for forestry operations in national parks [18].

For instance, 40 years ago London Bus and other vehicle operators used castor oil based fluids in rear axles gaining significant advantage in fuel consumption due to the excellently low coefficient of friction [19].

2.5.2 Limitations and current solutions for biobased lubricants

The use of biobased lubricants has some limitation properties. In this section the limitations and possible solution methods are described. The limitations are:

- Oxidative stability
- Narrow Viscosity Range
- Low Temperature Solidification

2.5.2.1 Oxidative stability

When lubricants are exposed to air, or oxygen, by help of heat, chemical reaction occur which lead to the deterioration of the oil as an increase in viscosity and some change in chemical properties. The oxidation leads to a deterioration of lubricant performance and can cause damage in the usage place [20].

As the nature of vegetable oil oxidates rapidly. For the use of the biobased lubricants, oxidative stability problem has to be solved.

Allylic hydrogens within vegetable oil molecules are susceptible to removal by radicals and substitution reaction to give hydroperoxides as the initial oxidation products. Secondary reactions of the hydroperoxides following the initiation oxidation reaction give many undesirable reactions include hydrogen abstraction, addition reaction, fragmentation rearrangement, disproportiation reaction and polymerization [2].

Most of the researches on the bio based lubricants are focused on the improvement of the oxidative stability. The main solutions to make more stable lubricants are below:

- Biotechnology to produce genetically modified oil**.** It is understood that higher oleic and lower linoleic acid makes the oil more stable. One way of doing this is using genetically modified seeds. DuPont has developed a genetically modified soybean that produces high levels of oleic acid. High oleic soybean oil lasts much longer than conventional soybean oil or canola oil. In researches it is investigated that genetically modified soybean oil degrades 27 times longer than unprocessed soybean oil. The major problem is the price of these genetically modified soybean oil. For the reason of the patented formulas these price is extremely high. This affects the price of the lubricants using genetically modified soy bean oils. Also another problem is the harvesting areas of the genetically modified soybean oils. Food grade soybean oil producers require isolation for the genetically modified farms from the food uses [21, 22].

- Nontransgenic modification to produce more stable oil. Development of new varieties with superior oil traits using genes from wild and commercial soy varieties. Among the new varieties being developed are those with higher levels of oleic acid and lower levels of saturated fats.
- Modification of the oil through chemical or mechanical processing to improve oxidative stability. Bio based esters are available with high oxidative stability. Generally, oxidative stability increases as the number of fatty acid chains per molecule decreases. Also it is found that esterifying soybean oil fatty acids with di- or mono-hydroxy alcohols increased oxidative stability, compared with glycerol esters. Also some attempts have been made to improve the oxidative stability by transesterification of trimethylolpropane and rapeseed oil methyl ester by selective hydrogenation of polyunsaturated C=C bonds of free acid chains [23].
- Chemical additives that improve stability offer the most rapid and cost-effective route to commercialization. The commercial additive antioxidants work in two different ways. One type acts as a free radical scavenger. The scavenger antioxidant converts available free radicals to non-radical products, eliminating their availability to polymerize. Antioxidants include organic compounds like hindered phenols and aromatic amines that acts as free radical scavengers. Another type suppresses the hemolytic breakdown of the chain structures, preventing the formation of radicals species with reactive sites. Organic phosphates belong to this category [16].

2.5.2.2 Narrow viscosity range

In terms of ISO VG (International Standards Organization Viscosity Grade) the vegetable oils cover only ISO VG 32 and 46. These range viscosity can only cover turbine, circulation and hydraulic system applications. For the applications which require higher viscosity values vegetable oil can't be suitable even when with the use of thickeners [2].

But apart from other vegetable oils Castor oil has a significantly high viscosity value then other vegetable oils. It might be for the reason of castor oil which is composed of esterified ricinoleic acid (>88%), which can be classified as hydroxyl monounsaturated. Apart from Castor Oil, hydroxyl group is not available in vegetable oils [23].

2.5.2.3 Low temperature solidification

The lowest temperature of oil still flows is called pour point temperature. As shown in the Table 2.6 pour point vegetable oils is much higher than most of the mineral oils. This makes it difficult to operate under cold conditions or in the cold start of engines. Problem can be solved by using available commercial additives but on the other hand using additive will affect the cost of the lubricants. Commercial additives usually consist of polymethacrylates, vinylacetates, styrene ester and etc [5].

One of the solutions to occur more stable lubricants hydrogenation of vegetable oil is used. But as far as the hydrogenation take place, pour point of the lubricants increases. To prevent the increase of the pour point, the hydrogenation has to be stopped at a certain level.

2.5.3 Biobased lubricant market

As it is previously explained, limited data is available for the biolubricant market. Only limited data is available for Europe and European Union countries. Even with the most of the lubrication market is on mineral based lubricants, the production of rapeseed or sunflower based lubricants has become attractive for the reason of quality and lubricity properties for years.

The biobased lubricant has gained importance for the reason of their environmental view. The lubricant market is forced to use biobased lubricants by legislations. First focus is gained on lubricants which are used in nature and have possibilities to spill to environment. The first ecolabel environmental award for lubricants was the Blue Angel which describes the chain saw lubricants in Germany in 1988. This is followed by concrete mould release oils and then Scandinavian countries (the White Swan) and Canada (Mapple Leaf) have gained the ecolabel awards [19].

By the help of the ecolabels the biolubricant have increasing volume growth in European lubricant market (See Figure 2.7).

Table 2.7: Recent European Market Volumes and Growth Rate [9].

Product Type	1999 European Volume (thousand tons)	2005 European Volume (thousand tons)	Annual Growth (%)
Lubricants	5000	4920	-1.4
Biolubricants	102	112.2	10
Synthetics	305	323.3	6
Synthetic Esters	80	84	5
Additives	600	600	0

2.5.4 Usage of biobased lubricants

The places where lubricants have possibility to contact with human, food and water sources are the most urgent areas to change to bio based lubricants. The first researches are done for the use in two stroke marine engines in national parks. Also the places where total lost of lubricants; especially chain saw lubricants and metal-working fluids have to be changed to more environmentally friendly ones. The most important usage areas of biolubricants are below:

- Hydraulic Fluids
- Greases
- Marine Lubricants
- Total Loss Lubricants
- Engine Oils

2.5.4.1 Hydraulic fluids

Hydraulic oils are widely used in pumps, turbines and propellers. Large amounts of hydraulic oils disappear every year during use. Great amounts of hydraulic oils are used and a big amount of it was disappeared every year by leakage, evaporation etc. Disappear of hydraulic oils contaminates ground water, poisons animals and plants.

Especially in forestry, many machine users have shown increasingly environmental concern. They have asked better oils for environmental and health point of view. To increase the usage of environmentally friendly lubricants some disadvantages of the oils have to be solved [24, 25].

The hydraulic oil market requires:

- More stable viscosity grade even at low temperature.
- Better oxidation stability
- Lower cold flow filtering point of oil
- With high upper temperature usage limit.
- More environmentally friendly oils.

Solving these requirements can increase the environmentally friendly hydraulic fluid usage [24, 25].

2.5.4.2 Greases

Lubricating greases can be defined as solid to semi-fluid products of the dispersion of a thickening agent in a liquid lubricant. The thickening agent is usually a metal soap. Generally, greases contain 65- 95% (w/w) base oil, from 5- 35% (w/w) thickeners and 0-10% additives.

The usage of the greases is gone till 3500 to 2500 BC in Sumerians on wheeled vehicles. In those times tallow or vegetable based oils are used as greases.

Even when mineral oils took predominant, most of the thickeners and additives remained environmentally acceptable.

Today’s used greases have to be change with more environmentally friendly ones especially in total loss applications or when there is direct contact with environment. Researches for producing more environmentally friendly base oils and thickeners are continuing. For today only rapeseed oil is introduced as base oil and calcium 12-hydroxystearate is introduced as environmentally friendly thickener in central Europe [2].

2.5.4.3 Marine lubricants

One of the biggest environmental problems about lubricants are for the reason of the use of two stroke engines in marine motors. Especially, the use of marine low biodegradable lubricants in national parks occur unfixable problems in nature.

Almost all lubricants that are used in two stroke engines are total loss lubricants. They are added to the fuel with a ratio of 150 to 1400 and burned in the fuel. But 30% of this lubricant is sent out from the exhaust unburnt and released to environment. Not only unburnt lubricant pollutes the environment, but also the polymeric combustion products give damage also [2].

The first test is done in Germany in national parks and all the lubricants are changed with the more environmentally friendly one.

2.5.4.4 Total loss lubricants

The biggest environmental pollution occurs in the applications where all the used lubricants are loss in the environment. The applications like metalworking lubrication, Chainsaw lubrication and two stroke engine lubrications are total loss lubrication methods.

In the applications like chainsaw lubrication and metalworking lubrications cutting fluids are used. These lubricants are required to have anti-wear property good penetration to the cutting zone and cooling property to avoid any wear on the cutting surface. Two stroke engine applications are described in marine lubricants chapter.

2.6 Engine Oils

Commercially, engine oils occupy 60% of the overall lubricant and functional fluid market. For the reason of the increase in the sales of the vehicles not only in Europe but also in third world countries as China, India and Korea, the demand for engine oil will increase in the future. The main purposes of use of engine oils are lubrication of engine, stabilize the compression, clean up and cool the engine. The vehicle engines can be described into two categories [26, 2].

In passenger car engines includes all gasoline and light diesel engines with direct of indirect injection. The engine oils for passenger engines are required to have good oxidative stability with good viscosity grade.

In commercial vehicle engines which includes trucks, buses, tractors, harvesters, construction machines and stationary machinery which are powered by diesel engines. These engines are highly turbocharged direct injection motors. These motors are required to have long life and to be reliable. Performance is also important for engine oils which are used in these types of engines. Heavy duty lubricants require having good wear property, long life and good viscosity grades [2].

2.6.1 Four stroke motorcycle oils

The design of the four stroke engines are mainly used in more performance required application in motorcycle like races. The lubricants of these machines are subject to numerous constrains then four stroke engines. So simple four stroke engine lubricants may not fulfills the requirement for four stroke motorcycle engine oils. The motorcycle engine oil is required to be good motor oil, transmission oil and coolant. In Figure 2.9 it is shown, the increase in the motorcycle use in Turkey. The increase in the use of motorcycles will lead to an increase in the requirement of lubricants [26, 2].

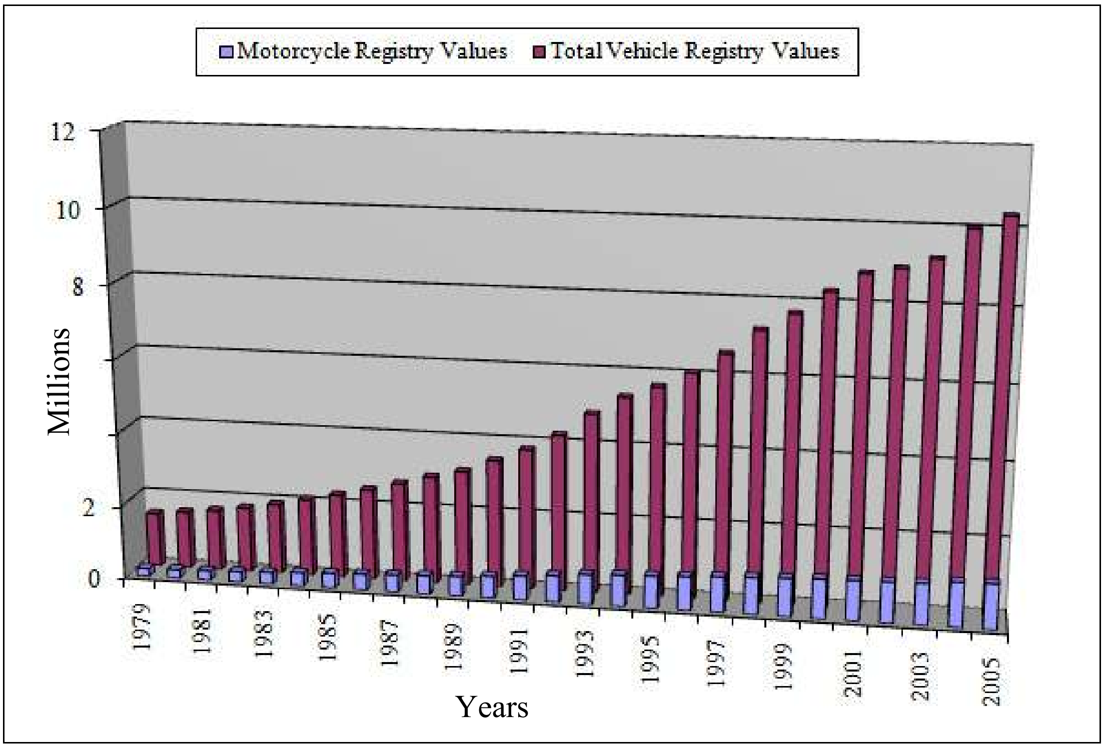


Figure 2.9: Turkey Motorcycle and Total Vehicle Sales Values in Years [27].

Commercially four stroke motorcycle oils which viscosities, viscosity index, density, total base number (TBN) are given are shown in Table 2.8.

One of the main constrains of the motorcycle engines are limitation of the placements. In these engines 40x40x60 cm area is filled with engine, clutch, gearbox, starting mechanism, electrical equipment, oil reservoir etc. The weight of these equipments is also an important feature as is the distribution of the weight in a machine is basically in unstable equilibrium. The weight of the motorcycle is up limited with 250 kgs.

In Figure 2.10, a commercial 4 stroke motorcycle engine is shown. By the limited area lubricants for four stroke motorcycles are required to lubricate the following components [27]:

- The engine
- The primary transmission
- The clutch
- The centrifugal clutch
- The gearbox
- The back torque limiter
- The starter system, torque limiter sprang clutch.

- **The engine:** Normally simple automotive engine oils with the additives of wear corrosion oxidation detergency/dispersant, pour point depressants will be suitable for four stroke motorcycle engine oils. But with the more specific power output leading the higher internal temperatures, for this reason oils with low temperature viscosity rating of 10W are advisable.
- **The primary transmission:** The power is transmitted form engine crankshaft to clutch is normally by a transmission system. The power is transferred with a reduction ration of 12 at the time engine rotating speed of approximately 15.000 rpm. This becomes a relatively high load of power in the transmission systems. There is a possibility of film breakdown on lubrication. For this reason, again not less than 10W minimum viscosity range lubricants are required to prevent risk of breakdown of lubricating surface

Table 2.8: Commercial four stroke motorcycle oils [28, 29, 30, 31].

Motor Oil	Viscosity, cSt		Viscosity Index	Density 20°C kg/m^3	TBN mg KOH/g	Flash Point, °C
	40°C	100°C				
Mobil **Super S 10w40**	92	14.4	154	870	-	230
Shell **Adavance VSX 4 10w40**	94.3	14.4	-	882	-	206
Castrol **Power 1 4T 10w40**	89.6	13.7	155	873	9.7	210
PO **Maxima 10w40**	13.86	-	156	873	9.8	234

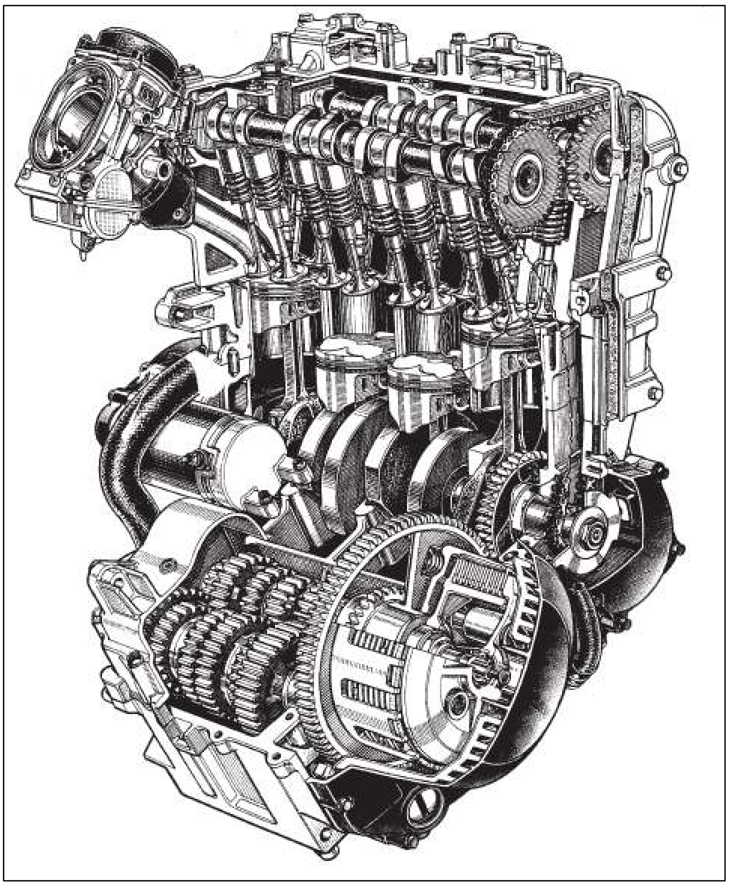


Figure 2.10: Kawasaki Ninja model ZX-6R motorcycle engine [27].

- **The clutch:** The clutch is designed to operate under control friction conditions. The clutch is consists of friction plates which are driven by engine and interspersed with metal plates which are driven by the primary gear shafts. Again viscosity is a critical data. Too high viscosity range can cause clutch to drag.

- **Gearbox:** The situation is same with the primary transmission. Again to high viscosity range can cause result in pitting of the gear teeth.
- **The centrifugal clutch:** The centrifugal clutches are used mainly in small engines and provide automatic transmitting of the power. If the friction coefficient between two sides of the clutch more rotating speed is required to shift the transmission. The presence of viscosity modifiers are required to prevent this problem.
- **The back torque limiter:** Between the shifts in the gear the power will improve progressively because of not having any intermediate between engine and the gearbox. For this reason generally torque limiter for back tire is used. This limits the engine power if it exceeds to a certain ratio.
- **The starter systems:** Especially when in the starting unlikely with the automotive engines there is a one-way drive clutch which generate heat and unlubricated. With certain viscosity improvers the increase in the temperature will reduce friction and will prevent then wear between surfaces.

2.7 Literature Review

In this section, literature review study under the theme of "alternatives for four stroke engine oils" is presented. Also selected studies from literature on biobased products, vegetable oil esters used as biobased lubricants are given in this section of the study. Limited papers are found about this subject.

Montgomery has studied the alternative uses of agricultural products, byproducts and coproducts. The alternatives are collected in five topics which are mainly:

- Bioremediation
- Use of fermentation byproducts
- Biocatalytic studies of corn and soybean
- Biochemical reactions which include biodiesel, biodegradable plastics productions
- Membrane technology in biobased products

In the research, Montgomery focused on the importance use of value added byproducts of agriculture by biosynthesized molecules found in agriculture instead of fossil fuel based chemicals which upsets the present natural balance [32].

Odi-Owei investigated the direct use of some vegetable oil and fats as lubricants. In his study he focused on ground nut oil and coconut oil and test the efficiency of lubrication with standard HD 90 gear oil. Tests were run under 4905 N at 8000 rev/min and results coconut oil and ground nut oil show 1.8-1.9, 2.3-2.9 times more life time then the reference gear oil respectively [33].

Kubo et. al. investigated the environmental lubricants and the research activities such as:

- Fuel efficient engine oils
- Biodegradable two-cycle engine oils
- Alternative refrigerants for refrigeration oils
- Chlorine free cutting oils
- Used oil recycling

The hydrorefined base oils and PAO uses in passanger car oils have importance to increase the fuel-saving performances. Also friction modifier additive uses have also environmental effect as fuel saving. Also in two stroke engine oils fuel efficiency performance can be increased by using low grade viscosity lubricants to increase the high shear stability in high temperatures and lower the friction force and also by using friction modifiers such as Molybdenumdithiocarbamate and zincdialkyl dithiophosphate to increase the fuel efficiency. For refrigeration oils polyalkylene glycols and polyolester usage instead of usage of toxic chlorofluorocarbons are suggested [34].

Filley investigated the synthesis and physical properties of cyclic acetals of methyl 9.10-dihydroxystearate.The viscosity grade of the cyclic acetals after the synthesis show that cyclic acetals are more likely to normal paraffin with the same number of non-hydrogen atoms. After the tests it is found that the cyclic acetals are suitable for fuel additive lubrication for the reason of low temperature solidibility effect [35].

Linko et. al. investigated the biodegradable compound production by using lipase (triacylglycerol acylhydolase, EC 3.1.1.3) biocatalysis. Biocatalysis reactions take place to produce 1-Butyl oleate, 2-Ethyl-1-hexyl ester, aromatic and aliphatic polyester [36].

Kulkarni et. al. investigated the use of Canola methyl ester/ ethyl ester system as lubricity additive for diesel fuels. 3:3 Methanol Ethanol blend is used in the presence of KOH catalysis and transesterified the canola oil. 90% of ester phase is recovered after reaction and by using 1% as additive in diesel fuel lubricity 0.979 lubricity number is achieved instead of having 0.781 lubricity number in base fuel [37].

Yunus et. al. investigated the trimethylolpropane ester on palm and palm kernel oil. The results are compared with the commercial hydraulic fluids and show increasing performance in viscosity index, wear and friction properties. Dispite their high pour point the products will be acceptable to use as alternative biodegradable lubrications [38].

Belluco et. al. investigated the performance of vegetable oils as cutting fluid instead of mineral based ones. The results are compared with part accuracy, surface roughness and microhardness. The overall results show that vegetable oils show better performance then mineral oils [39].

Dörmö et. al. investigated the solvent free system for environmental biolubricant production from fusel oil and oleic acid. Commerical lipase enzyme is used for biocatalyst. The biolubricant is compared with dicarboxylic acid ester. The results show that the thermal and oxidative stability is higher than reference lubricant [40].

3. EXPERIMENTAL PART

Aim of experimental study is, starting from mineral, synthetic and biobased lubricants; to prepare mineral, synthetic, biomineral and biosynthetic based four stroke motorcycle motor oils, to determine the lubricant and lubricity properties of the motor oils.

3.1 Materials and Methods

The mineral, synthetic, biobased oils and additives are used in this study. Light Neutral oil is used as mineral oil and supplied by POAS Company. Polyalphaolefins 6 (PAO 6) and Polyalphaolefins 10 (PAO 10) are used as synthetic base oil and supplied by SLS-Senturk Company. ME (ME) which is in the standards TS EN 14214 is used and supplied from CHS Company. Motor oil additives and viscosity index modifier (VI) additives are taken from SLS-Senturk Company with the commercial name as Hitec 9235 and Hitec 5748.

The motorcycle motor oil preparation and lubricant tests are done in Research and Development Laboratory in POAS Derince Plant, according to ASTM test methods.

The lubricant tests for motorcycle motor oils are done as viscosity, density, cold cracking simulation (CCS), total base number (TBN), total acid number (TAN), Sulphur Content, Water Content, Ash Content, Sulphonated Ash content, Carbon Residue, Shear Stability, Foam, Copper Corrosion, Pour Point, Flash Point and Fire Point tests.

10w40 motorcycle motor oils have the viscosity of 12.5- 16.3 cSt and 100°C and maximum 7000 mPa*s at -25°C of CCS test result in the API (American Petroleum Institute) standards. All the oil samples are prepared by adding base oils and additives at required percentages in a beaker and mechanically mix at 50°C for 45 minutes and cool to ambient temperature.

3.1.1 Lubricity Test

The lubricity tests of the samples are done in Isparta, Suleyman Demirel University at Mechanical Engineering Department Laboratory in the fixed forced lubricity test rig. The test equipment is designed in Suleyman Demirel University. The test rig was designed to test the variation of the friction force according to speed and loads in journal bearing. In the system the magnitude of load varies from 60N to 600N and the speed of were from 30 rpm to 1000 rpm. Before starting the test 6 lt. of lubricant is filled up in to oil tank. Before lubricants were fed to oil tank, it was cleaned by filtering. During the test the cooling system was placed at the end of oil tank to obtain constant temperature. Tests were carried out at lubricated conditions at the ambient temperature and 100°C.

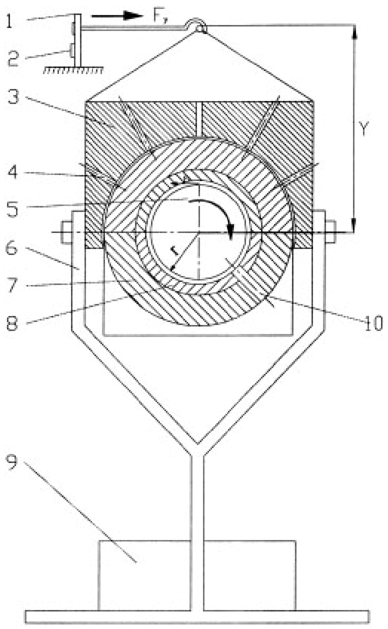
A commercial babbitt alloy bearing was used as the test bearing, which had a central circumferential groove. Four oil supply holes were placed in this groove. The diameter, width and clearance of the test bearing were 50.750 mm, 25.00 mm, and 0.050 mm, respectively. The journal (shaft) was made of SAE 1030 hardened steel with a Rockwell hardness of 55. One end of the journal was supported by two ball bearings that could carry both axial and radial loads. The journal is driven by a belt-driven pulley mounted over the steel journal and connected to an A.C. electric motor (1.1 kW), which could operate under different speeds. The journal was ground to a N4 surface finish quality and its average height of asperity (Ra) was 2 μm and the journal bearing had N4 surface finish quality with a height of asperity Ra = 3 μm. In order to prevent metallic contact between hydrostatic pad, on which the loads hanged, and journal bearing housing, a hydrostatic pocket was developed. Besides, six lubricating channels were used in order to provide a hydrostatic lubrication that could prevent contacts between lateral surfaces of hydrostatic pad and journal bearing housing. During the experimental study, any severe metallic contacts occurred between moving surfaces that were between hydrostatic pad with journal bearing housing and between journals with journal bearing were well controlled. Lubricating oil was provided for hydrostatic pad requiring oil by gear-pump. The same lubrication oil was used for both hydrostatic pad and test journal bearing.

The journal was rotated by running an electric motor. Due to the friction between the test bearing and rotating journal, the journal bearing housing turned in the same direction of journal. The steel rod that is connected with bolts up to the surface of journal bearing housing forced the steel spring that had rectangular cross-section to bend. Two straingauges were fastened at the top and the bottom surfaces of the steel spring. The reaction force (*Fy*) was applied on the bearing housing which was counterbalanced by the torque due to the friction force. *Fy* was the force that forced the steel spring to be bent. The latter force of friction (*Ff*) was determined by measuring the distance (*Y*) according to the reaction force (*Fy*).

$$F_y \cdot Y = F_{f.}\, r$$

$$\mu = F_f / F$$

The test rig (see Figure 3.1 and 3.2) is done at ambient temperature and 100°C at 1000rpm at 260 N for 45 minutes. The temperature is selected for the reason of testing ambient temperature start up and at running temperature. The maximum rpm is selected for the reason of the motorcycle engines running condition. To check the lubricity standard four ball lubricity conditions are selected as 260N for 45 minutes and Ff and μ results are shown in the graphs in results and discussion section [41].



1 : Steel Spring
2 : Strain-Gauge
3 : Hydrostatic Pad
4 : Hydrostatic Oil Supplies
5 : Journal (Shaft)
6 : Hanger of Load
7 : Bearing Housing
8 : Test Journal Bearing
9 : Load
10 : Oil Supply Test Bearing

Figure 3.1: Experiment System

Figure 3.2: Views of Experimental System

3.2. Preparation of Mineral, Synthetic and Bioblends for 10w40 Motor Oil

Mineral oil preparation is done according to SLS-Senturk Company formulation starting form Light Neutral and additives, MO content is [42]:

Light Neutral Base Oil	:	80.3	%
Viscosity Index Modifier	:	12.0	%
Motor Oil Additive	:	7.7	%

The viscosity, cold cracking simulation and the density results of mineral base oil which is shown in Table 3.1, that Light Neutral based motor oils is in the range of 10w40 motorcycle motor oil.

The viscosity at 100°C is in the range of 12.5 and 16.3 cSt and CCS is very near to required value which the difference is negligible.

Table 3.1: Properties of MO

Properties		MO
Viscosity, cSt	40°C	107.990
	100°C	14.947
Density, 20°C, kg/m^3		880.49
CCS(-25°C), mPa*s		7105

Synthetic motor oil preparation is done starting from PAO 6 and PAO 10. The additive contents are prepared according to SLS-Senturk Company formulations [42].

The first tests are carried on to decide the content of PAO in the motorcycle motor oils. Table 3.5 shows the change of viscosity with the change of PAO 6 and PAO 10 concentrations. Table 3.2 and Figure 3.3 show that, 6 different test results are suitable to produce 10w40 motorcycle motor oils. But for the further tests to produce more stable biobased blends upper limit of the test result are chosen. For this reason SO content is chosen as:

PAO6	:	32.3	%
PAO 10	:	50.0	%
Viscosity Index Modifier	:	10.0	%
Motor Oil Additive	:	7.7	%

Table 3.2: Change of Viscosity with Change of PAO Content

Synthetic Oil, %(w/w)		Additives, %(w/w)		Viscosity, cSt	
PAO 6	PAO 10	VI Modifier	Motor Oil	40°C	100°C
82.3	0	10	7.7	77.992	12.41
70.3	12	10	7.7	82.87	13.15
68.3	14	10	7.7	83.6	13.26
62.3	20	10	7.7	87.785	13.65
52.3	30	10	7.7	94.1	14.41
42.3	40	10	7.7	101.3	15.04
32.3	**50**	**10**	**7.7**	**109.6**	**15.94**
22.3	60	10	7.7	119.2	16.77
12.3	70	10	7.7	127.8	17.74
0	82.3	10	7.7		18.910

After the mineral and synthetic based 10w40 motor oils are prepared ME is blended and Biomineral motor (MOME) and Biosynthetic motor oil (SOME) are prepared.

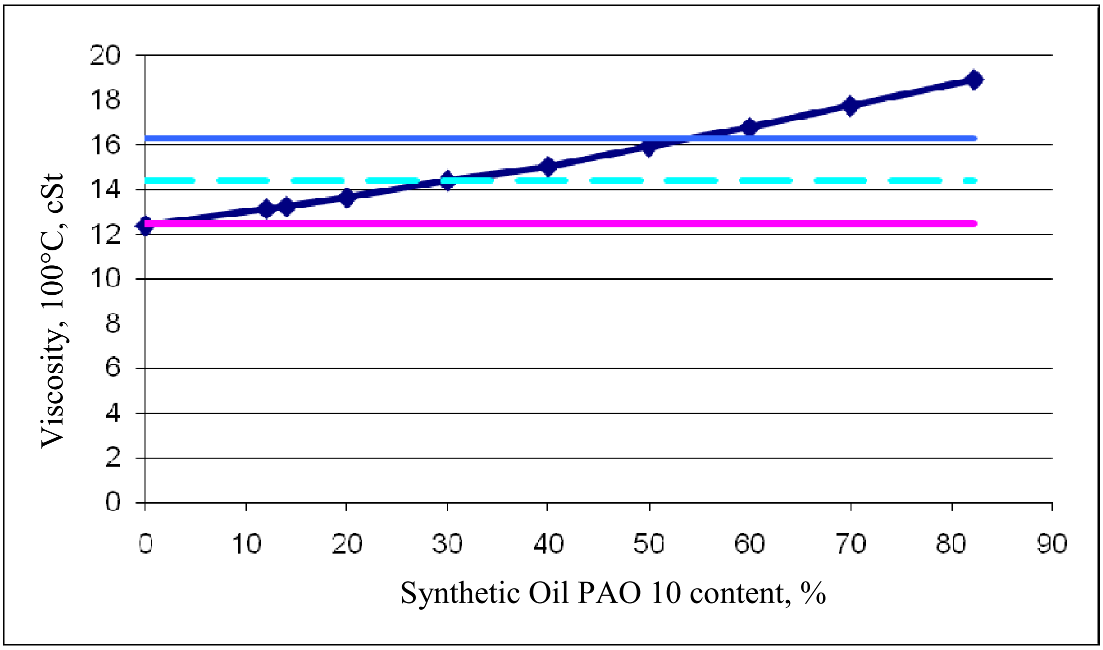


Figure 3.3: Change of viscosity with change of PAO 10 content

3.2.1. Biomineral based motor oil preparation

Biomineral based motorcycle motor oil is done by blending the MO which is light neutral base oil in our study and ME. The different concentrations of MOME are tested. Table 3.3 shows the viscosity and density change with the change of content of ME. In Figure 3.4, shows that only 3 concentration samples are suitable for 10w40 motorcycle motor oils. But, for more stable motor oils it is required that the 100°C viscosity have to be at the center point of the required viscosity range. For this reason the sample which has %5 ME content is chosen and MOME content became as:

Light Neutral Base Oil	:	75.3	%
ME	:	5.0	%
Viscosity Index Modifier	:	12.0	%
Motor Oil Additive Package	:	7.7	%

Table 3.3: Change of viscosity and density with change of ME content in MOME

Base Oil Type	Content, %(w/w)		Viscosity, cSt		Density, 20°C , kg/m^3
	Mineral Based	Biobased	40°C	100°C	
Mineral Based	80.3	-	107.990	14.947	880.49
Biobased	-	80.3	4.674	1.837	884.46
Mineral +Biobased	80.3	0	86.350	13.260	880.55
	75.3	5	69.900	11.512	880.56
	70.3	10	47.280	9.070	880.82
	60.3	20	32.850	7.161	881.14
	50.3	30	23.370	5.780	881.44
	40.3	40	17.050	4.663	881.85
	30.3	50	12.720	3.810	882.27
	20.3	60	9.640	3.160	882.72
	10.3	70	7.450	2.594	883.23

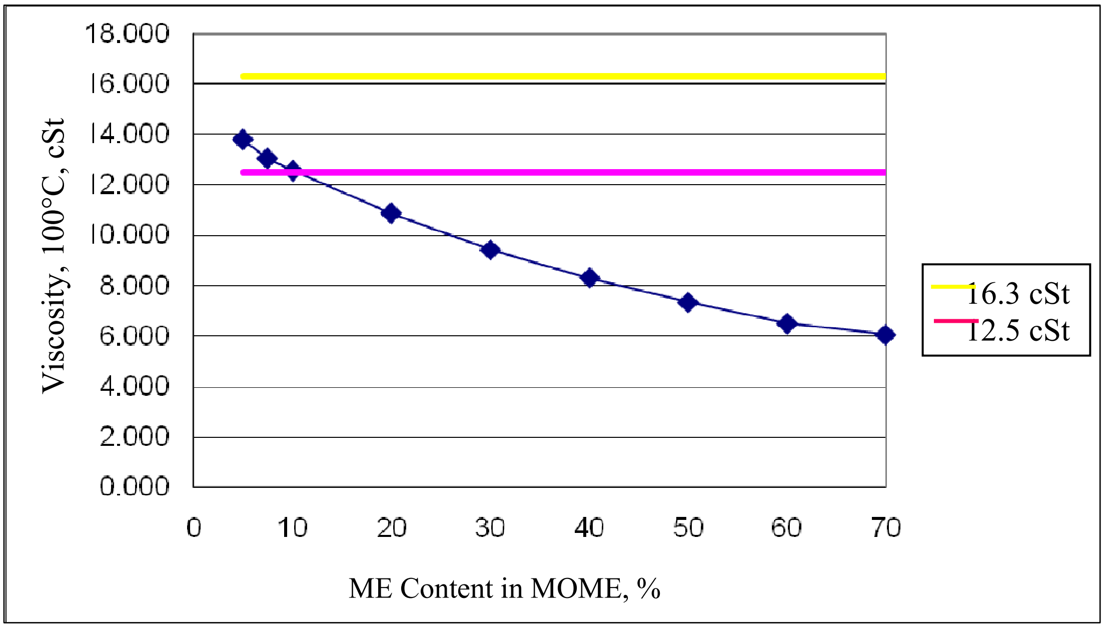


Figure 3.4: Change of viscosity with change of ME content

3.2.2 Biosynthetic based motor oil preparation

The selected SO and canola ME is used for the SOME production. The viscosity and density change with the change of biobased lubricant concentration is shown in Table 3.4. In figure 3.5 it is shown that 2 different concentrations are suitable to produce 10w40 motorcycle motor oil. But for more stable motor oils it is required that the 100°C.

viscosity have to be at the center point of the required viscosity range For this reason the sample which has %5 ME content is chosen and SOME content became as:

PAO6	:	: 30.3	%
PAO 10	:	: 47.0	%
ME	:	: 5.0	%
Viscosity Index Modifier	:	:10.0	%
Motor Oil Additive Package	:	:7.7	%

Table 3.4: Change of Viscosity and Density with Change Of ME Content In SOME

Base Oil Type	Content, %(w/w)		Viscosity, cSt		Density, 20°C, kg/m^3
	Biobased	Synthetic Based	40°C	100°C	
Synthetic+Biobased	**5**	**77.3**	**91.6**	**14.38**	**847.73**
	10	72.3	78.7	13.17	850.24
	15	67.3	69.6	11.99	852.66
	20	62.3	58.67	11.058	855.25
	30	52.3	44.86	9.41	859.95
	40	42.3	35.84	8.16	862.26
	50	32.3	27.46	6.98	871.26
	60	22.3	22.7	6.024	876.65
	70	12.3	20.5	5.36	880.52
	82.3	0	13.97	4.55	889.66

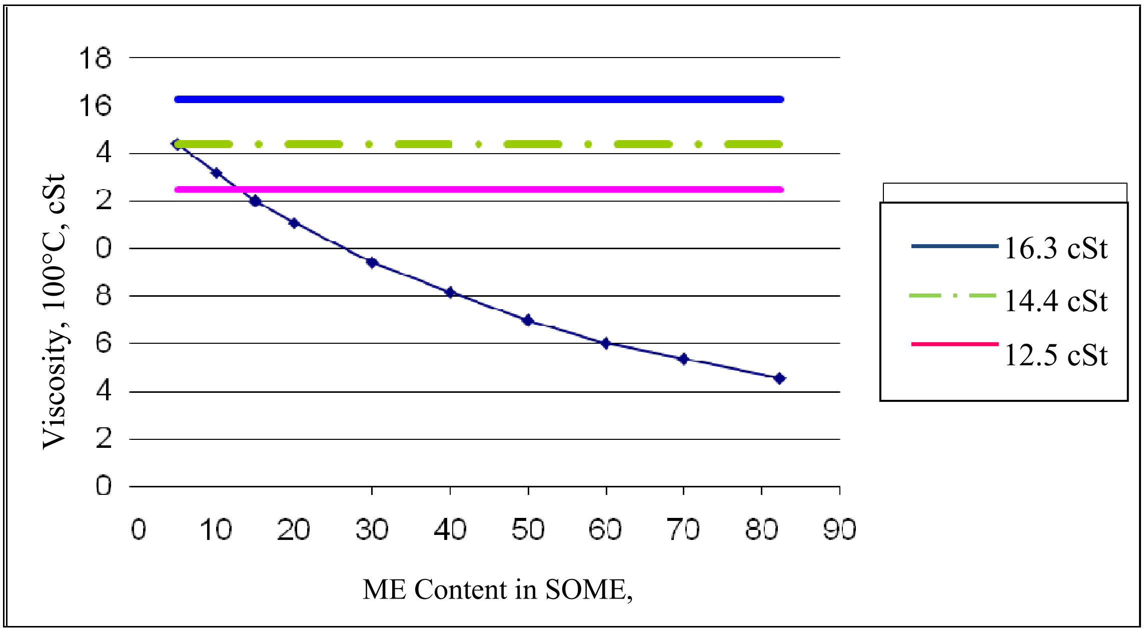


Figure 3.5: Change of Viscosity with Change of ME Content in SOME

4. RESULTS and DISCUSSION

In this section, results of experimental studies on motor oil selection, motorcycle motor oil tests and lubricity test results are described respectively.

- Properties of motor oils
- Lubricity test results for motor oils

4.1. Properties of Motor Oils

In the previous section mineral, biomineral, synthetic, biosynthetic motorcycle motor oils are chosen and produced. The contents of motor oils in the study are shown in Table 4.1.

Table 4.1: The Content of the Motor Oil Samples

Motor Oils	Biobased	Mineral Based	Synthetic Based		Additive	
	ME	Light Neutral	PAO 6	PAO 10	Motor Oil Additive	VI modifier
MO	-	80.3	-	-	7.7	12
MOME	5	75.3	-	-	7.7	12
SO	-	-	32.3	50	7.7	10
SOME	5	-	30.3	47	7.7	10
ME	100	-	-	-	-	-

The content of mineral, biomineral, synthetic and biosynthetic motor oils is selected in section 3.2 and 3.4, motor oil tests are shown in Table 4.2. The properties of the motor oils show us the results that:

- Viscosity of biomineral and biosynthetic ester is less than the viscosity of mineral and synthetic ester. This is for the reason of MEs viscosity.
- The improvement of the cold cracking values can be seen between mineral, synthetic lubricants and biomineral and biosynthetic lubricants.

Table 4.2: Properties of Motor Oils

Properties		ASTM Test Method No	MO	SO	ME	MOME	SOME
Viscosity, cSt	40°C	D 446	109.6	14.947	4.674	92.41	91.6
	100°C	D 446	15.94	107.99	1.837	13.79	14.38
Density, 20°C, kg/m^3		D 1298	0.88049	0.84662	0.88446	0.88107	0.84773
CCS, mPa*sec -25°C		D 5293	7105	5213	-	5952	3697
TBN, mg KOH/g		D 2896	7.8568	7.6213	0	7.8011	7.6213
TAN, mg KOH/g		D 974	2.688803	2.515219	0.798779	2.686351	2.387157
Sulphur Content,%		D 2622	0.0743	0.02504	0.000011	0.0714	0.02517
Water Content, ppm		D 4007	1346.26	1645.49	744.93	1448.96	2228.86
Ash Content, % (w/w)		D 482	0.005938	0.005349	0	0.004677	0.003588
Sulphonated Ash, % (w/w)		D 874	0.007794	0.007561	0	0.007687	0.007729
Carbon Residue, % (w/w)		D 524	0.141225	0.011036	0.032945	0.113751	0.014239
Shear Stability, % (w/w)		D 6278	12.16398	10.14402	0.25641	9.071118	8.134642
Foam, ml		D 892	10/0	5/0	5/0	10/0	5/0
Copper Corrosion		D 130	1A	1A	1A	1A	1A
Pour Point, °C		D 97	-21	-51	-39	-21	-51
Flash Point, °C		D 93	236	258	186	230	240
Fire Point, °C		D 93	256	288	210	246	276

- The flash point and fire points are reduces for the reason of ME low flash and fire point in addition of ME.
- TAN and TBN values have slight changes in addition of ME because of using unused base oils and same additives.
- Sulphur content of the motor oils decreases with the addition of ME because of the low sulphur content of ME. This is the main reason of biobased lubricants to be ecologic.
- Sulphonated ash and ash values changes in the motor oil mainly with the change of additive. In our study content of motor oil additives are same. For this reason only slight changes can be seen in the results.
- The shear stability test shows us that the synthetic based motor oils have the biggest change in viscosity after cutting. This is for the reason of the breakdown of the polymeric compounds in the base oil. The mineral based motor oil has less change in the viscosity then the synthetic based ones. By the addition of biobased lubricant in the mineral and synthetic lubricant, the improvement in the shear stability can be seen. This shows that by addition of biobased compound, the lubricant become more stable.
- Copper corrosion and foam results of the motor oils are same. This is because of wear and antifoam additive content in the motor oil lubricant additive package.

4.2. Lubricity Test Results of Motor Oils

In Figure 4.1 it is shown that the friction force in synthetic and biosynthetic motor oil increases with the increase of temperature. A slight difference can be seen in ambient temperature friction force between synthetic motor oil and biosynthetic motor oil. It is also seen that the difference between biosynthetic motor oil at ambient to 100°C is greater than synthetic oil friction force difference. This is for the reason of the friction force change in the ME at 100°C.

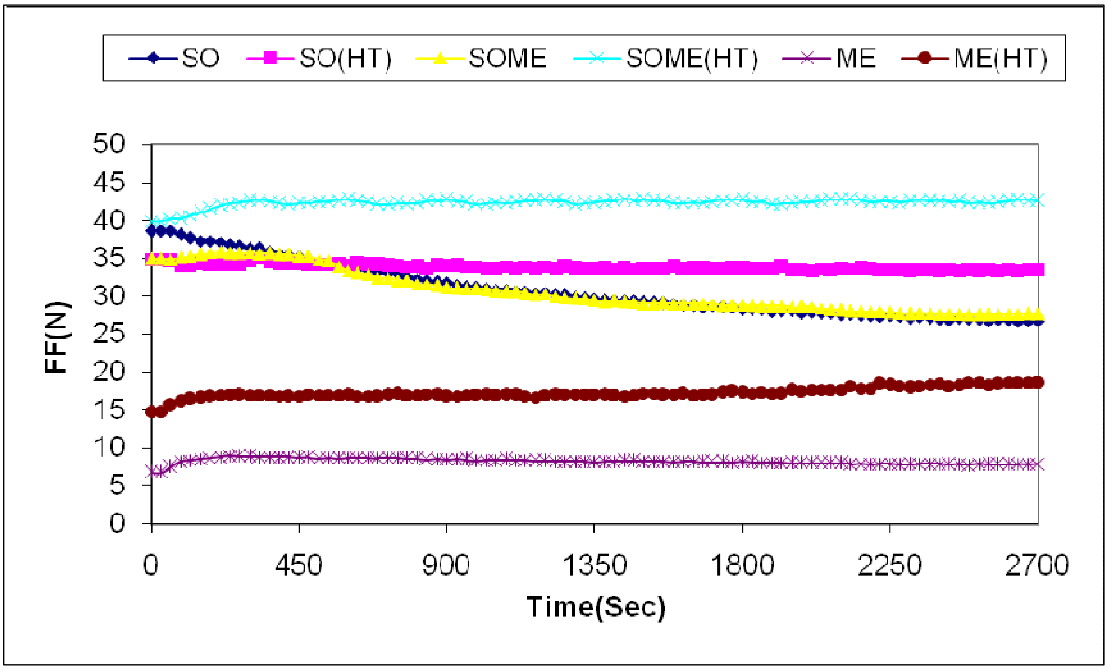


Figure 4.1: Friction force of SO, SOME and ME at ambient temperature and 100°C

In Figure 4.2 it is shown that the friction force in MO and MOME increases with the increase of temperature. ME content effect the friction force in the MO and this can be seen from change in the friction force between MO to MOME both in ambient and 100°C. The friction force difference between MOME in ambient and 100°C is for the reason of decrease in the viscosity for the reason of ME content. In Figure 4.3 it is shown that the friction force slightly decreases with the addition of ME content to SO.

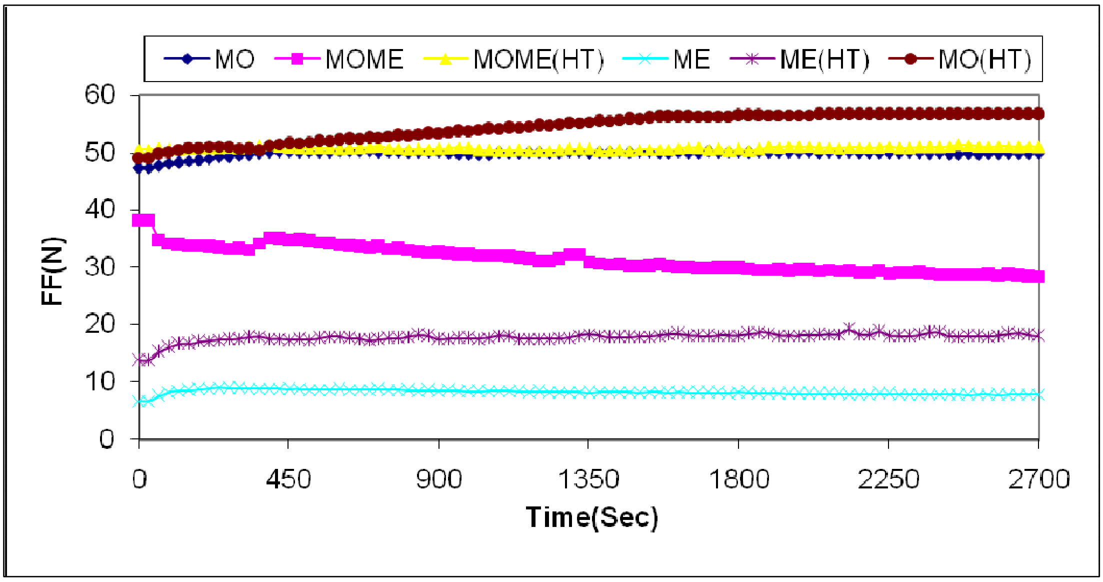


Figure 4.2: Friction force of MO, MOME, ME at ambient temperature and 100°C

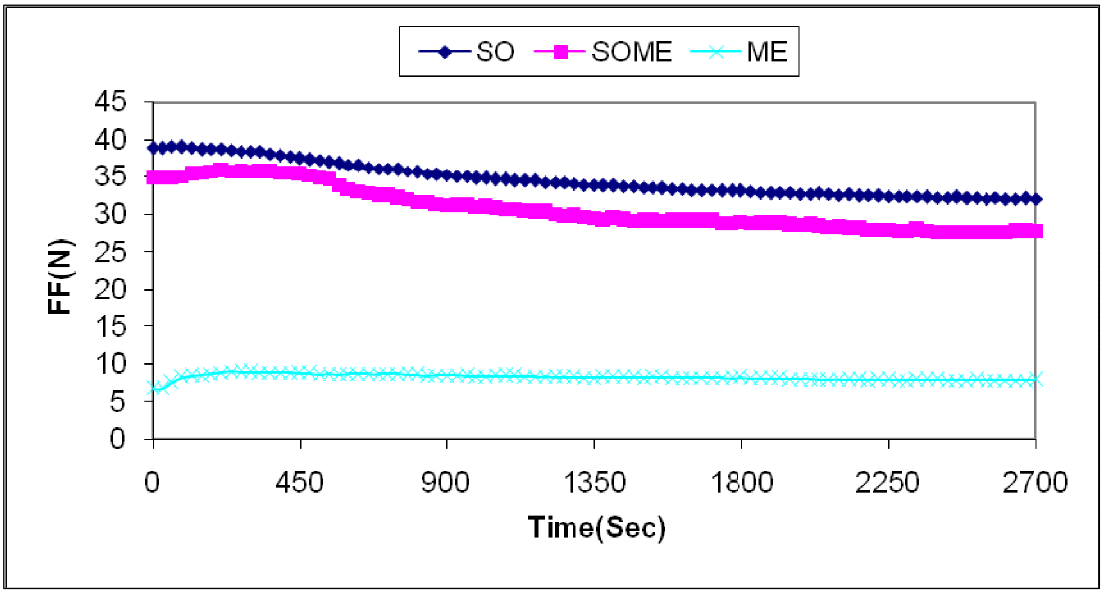


Figure 4.3: Friction force of SO, SOME and ME at ambient temperature

In Figure 4.4 it is shown that the friction force decreases with the addition of ME content to MO. In Figure 4.5 it is shown that the friction force decreases with the ME content both in MO and SO. But the decrease in friction force is greater in MO because of SO is a more stable lubricant than MO. It is seen that SOME has the best friction force in ambient temperature.

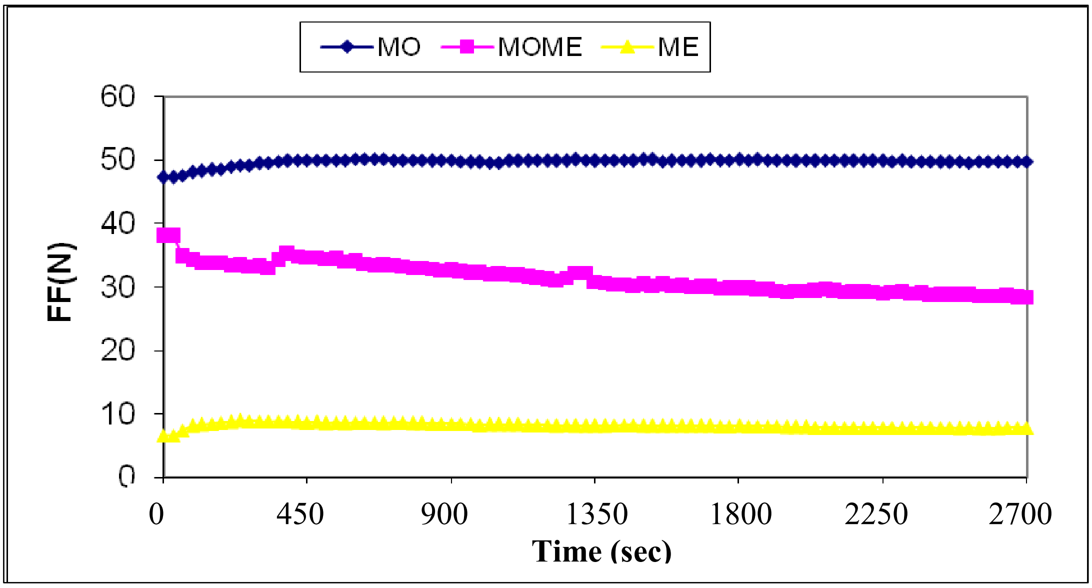


Figure 4.4: Friction force of MO, MOME and ME at ambient temperature

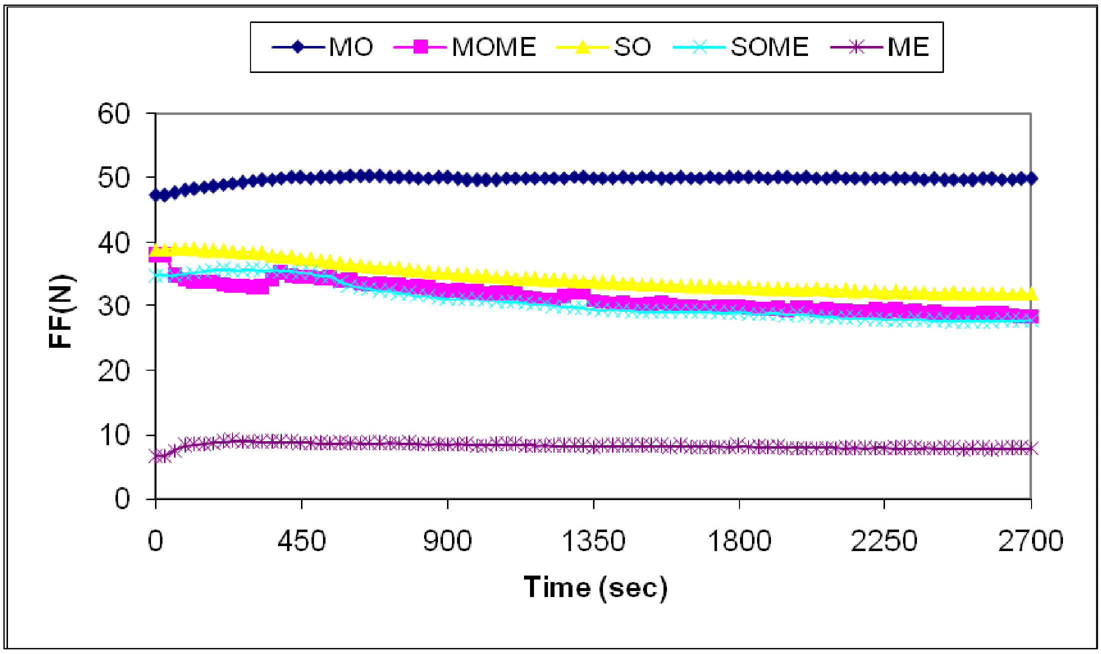


Figure 4.5: Friction force of MO, MOME, SO, SOME, ME at ambient temperature

In Figure 4.6, it is shown that SO has the best friction force in high temperatures. A slight increase can be seen from synthetic to SOME. This is for the reason of the ME contents viscosity decrease.

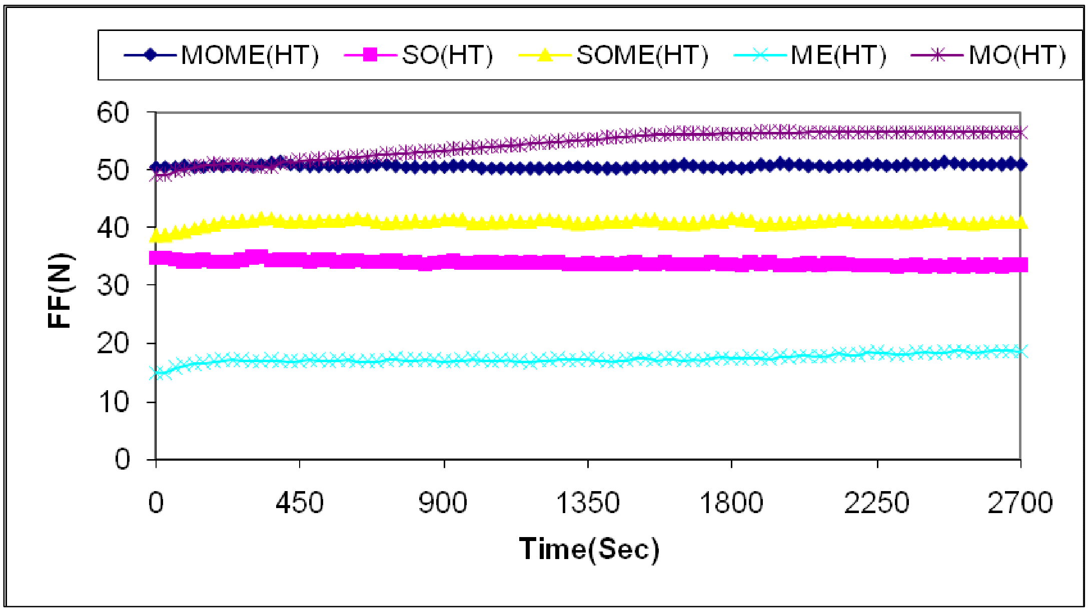


Figure 4.6: Friction force of MO, MOME, SO, SOME and ME at 100°C

5. CONCLUSION

In this study, alternatives for four stroke 10w40 motorcycle engine oils are investigated. mineral, biomineral, synthetic, biosynthetic based motorcycle motor oils are prepared, lubricant properties and lubricity values are determined. As a result of experimental studies, following results were obtained:

- For four stroke motorcycle motor oils up to 5% of canola methyl ester can be blended to the mineral or synthetic based motor oils due to low viscosity.
- Viscosities of biomineral and biosynthetic motor oils have less viscosity then mineral and synthetic ester. This is for the reason of canola methyl esters viscosity.
- The cold cracking values improve with the blend of biobased lubricants into the mineral or synthetic based lubricant, this lead the motor oil to work with bigger range of standards.
- The flash and fire points of biosynthetic and biomineral lubricants are less then mineral and synthetic lubricants.
- The best lubricity values for motor oils can be seen from biosynthetic lubricants at ambient temperatures.
- The lubricity tests under 100°C have higher friction forces then ambient temperature friction forces of motor oils.
- The synthetic based motorcycle motor oil has the least change of friction force with respect to temperature.
- The biosynthetic based motorcycle motor oil has slight bigger friction force then synthetic motorcycle motor oil at 100°C for the reason of viscosity change.
- 5% of usage of canola methyl ester in motorcycle motor oil will have advantages of using national renewable resources then importing crude oil, increase in the employment and have good affect on national economy.

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