SYSTHESIS OF GREASE FROM CASTOR OIL

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ABSTRACT

The aim of this research is to prepare base oil and thickener for grease formulation. Base oil was synthesized from the epoxidation of castor oil using 2.78 mol of hydrogen peroxide, 0.70 mol of acetic acid, 0.10 mol of castor oil, and 0.03 mol of H_2SO_4 followed by the ring – opening reaction of epoxidised product by water and acetic acid presented in the reaction mixture. The reaction temperature for peracetic acid preparation and for epoxidation was 50°C and room temperature whereas the reaction time for peracetic acid preparation and for epoxidation were 4 and 15 hours, respectively. The products were characterized by ^1H NMR spectroscopy. It was found that double bond was totally oxidized and epoxidised ring was also totally opened with 84% of water and 16% of acetic acid. For grease formation, sodium soap was used as thickener. Four samples of grease were formulated by using the oil/soap ratio of 90:10, 80:20, 70:30, and 60:40. The grease with 90 to 10 ratio and 80 to 20 ratio were not thick enough. The other grease samples were subjected to the dropping point test and cone penetration. It was found that the dropping point of grease with 70:30 and 60:40 ratios were 106°C and 109°C, respectively.

Moreover, the cone penetration of grease with 70:30 and 60:40 ratios indicated that they could be classified according to NLGI as grade 4 and 5 uses as hard grease or in rolling contact bearing.

Keyword: Base oil, Thickener, Grease, Castor oil

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ABBREVIATIONS

°C : degree Celsius

ASTM : American Society for Testing and Materials

NLGI : National Lubricating Grease Institute

ppm : parts per million

cSt : centistokes

mL : milliliter

in. : inch

s : second

δ : chemical shift

% wt : percent weight

Chapter 1

Introduction

1.1 Background [1-5, 11]

Lubricants can be classified into 2 types which are lubricating oils and greases. Greases are a semifluid to solid mixture of base oils and thickeners. Historically, it has been found that animal and vegetable oils were used as lubricants in general transportation or machinery to reduce friction that has the benefit of reducing heat generation and wear, transfer heat and carrying away of contaminants to filter and removal. However, they are inadequate for industrial applications because of low quantity of their volume and desirable properties.

The most favorable lubricating base oil is mineral base oils from petroleum because of the low price, high quality, and good stability comparing with vegetable oils. However, reservoirs of petroleum oil are limited and may be exhausted by the end of the next century. Recently, vegetable oils have been once again concerned because they are made from renewable resources which are environmental friendly. In generally, vegetable oils are non-toxic and unsaturated compounds which have excellent properties to easily react. Properties of vegetable oil could be adjusted by using epoxidation reaction to form epoxide ring, followed by the ring opening reaction using alcohols to expand hydrocarbon branch chains to become desirable ester oil. Synthetic esters are now used in many applications including grease formation. Greases from synthetic ester can be characterized by outstanding thermal and oxidation stability, low volatility, and high viscosity index. For example, ENS Grease is a long-life roller bearing grease with excellent properties at both low and high temperatures. It is blended from organic urea thickener and synthetic-ester base oil. The thickeners in ENS Grease are urea compounds, so the grease has a high dropping point and little oil separation. ENS Grease has low water washout, so it is very resistant to water.

The chemical composition of castor oil is listed in Table 1.1. Ricinoleic acid which has one double bond is the main fatty acid composed in castor oil molecular structure. Castor oil is chosen as model compound for epoxidation reaction in this work. It is because of its high percentage of double bonds. Castor oil can be epoxidised to form epoxide rings. The procedures used in this work was an adaptation according to the research previously done by T. Wattanakul and V. Chuenchom which synthesized 9,10-epoxystearic acid by epoxidation of oleic acid with peracetic acid generated from hydrogen peroxide and acetic acid in the presence of H_2SO_4 catalyst. Epoxide rings was then opened to form branch chains which help in adjustment of the properties. The percentage of double bond epoxidation and ring- opening reaction was studied by NMR spectroscopy. Preparation of greases using the oil product with sodium soap of palm oil will be attempted. The suitable formulation of grease was determined. Some properties of the synthetic of ester and grease, such as dropping point and cone penetration were also tested.

Table 1.1: The chemical composition of castor oil [3]

Name	Notation	% Composition in castor oil
Oleic	18:1 (9C)	8
Linoleic	18:2 (9C, 12C)	-
∝ —linolenic	18:3 (9C, 12C, 15C)	3
∝ —eleostearic	18:3 (9C, 11t, 13t)	-
Ricinoleic	18:1 (9C) 12-OH	86
Plamitic	16:00	-
Stearic	18:00	2

1.2 Objectives

1. To synthesize an ester product, the ring-opening derivatives of epoxidised castor oil, from the reaction of castor oil with acetic acid and hydrogen peroxide.
2. To prepare grease from the synthesized ester and sodium soap from palm oil.
3. To test the properties of synthesized ester and grease according to ASTM method.

1.3 Scope of study

1. Epoxidation reaction of castor oil with peracetic acid generated from the reaction between glacial acetic acid and hydrogen peroxide (using sulfuric acid as catalyst) to synthesize epoxidised castor oil and the synthetic ester. Characterization of products used ^{1}H NMR spectroscopy technique.
2. Saponification of plam oil and NaOH solution to produce sodium soap.
3. Preparation of grease by blending synthetic oil with the soap mixture by varying soap/oil ratio from 60:40 to 70:30 to 80:20 and 90:10.
4. Determination of the physical and chemical properties of the synthetic oil according to ASTM method such as viscosity at 40°C, viscosity at 100°C, and viscosity index.
5. Determination of the physical and chemical properties of the synthetic grease according to ASTM method such as dropping point and cone penetration.

1.4 Expected Results

Greases of good properties can be prepared by mixing sodium soap from palm oil with ester oil prepared from epoxidised castor oils.

Chapter 2

Theory and literature reviews

2.1 Lubricating grease [6]

Lubricants are used to reduce the friction when two objects in contact are moved relative to each other. It also reduced the demand for muscle power. In the ancient transportation sector, animal fats were used in conjunction with inorganic fillers to reduce the frictional forces between the bearing surface and shaft on chariot wheels.

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 and the transition of lubricating greases is fluid. There are two sides of thickening agent ; the first one is liquid side which oil containing less than 5% w/w thickening agents they are already having structural viscosity but not get a yield point yet. Therefore they have been named non-fluid oils. The second one is solid side which suspensions greater than 40%w/w solid lubricants in oils are usually called pastes. When greases contain both thickening agent typical of greases, they are also called grease pastes. Nevertheless, greases in general contain from 65-95%w/w base oils, from 5 to 35% thickeners and from 0-10% w/w additives.

Greases have been named in way they have used, e.g. still mill greases for after the kind of application, will bearing greases for after their prevalent application temperature, low temperature greases for after their range of application, and multi- purpose greases. The meaning of the latter has changed with the years and the other names do not say much about the quality of the performance of the grease.

The consistency of a solid to semi-fluid body is a very complex subject, but the penetration of one body into another one can be measured easily and with simple devices. Greases are named according to the consistency classes defined by the US national lubricating grease institute (NLGI) in 1983 and in accordance with the cone-penetration method developed in 1925 as shown in Table 2.1.

Nowadays the performance of lubricating greases is described by norms such as ISO 6743-9 or DIN 51825 defining mainly consistency, upper and lower operating temperature, water resistance, and load – carrying capacity, and for automotive greases by ASTM D4950, which has been followed by the consideration of reference grease and the introduction of the NLGI certification mark.

Table 2.1 : Classification of greases by NLGI numbers [6]

NLGI number	Appearance	ASTM worked penetration (1/10 mm)	Application
000	Fluid	445-475	Use in low viscosity applications including enclosed gear drives operating at low speeds and open gearing
00	Semi-fluid	400-430	
0	Extremely soft	355-385	
1	Soft	310-340	
2	Creamy	265-295	Greases for bearings
3	Firm	220-250	Use in rolling contact bearings
4	Very firm	175-205	
5	Hard	130-160	Hard greases
6	Soap-like (very hard)	85-115	Block greases

2.2 The Composition of Synthetic Grease [6]

Grease consists of two fundamental components: a base fluid representing the principle ingredient in the formulation and a thickening agent that is used to immobilize the fluid. The concentration of the thickener determines the consistency of the finished product; however, it is the nature of the oil that determines whether the grease will be classified as a synthetic. The lubrication oils commonly used to formulate synthetic lubricating greases as listed in Table 2.2

Table 2.2: Lubricating oils commonly used in synthetic greases [6]

Fluids	Characteristic
Diesters	Suitable for making grease serviceable to -73°C (-99°F)
Polyol esters	Higher viscosity than the diesters with better oxidative stability and less volatility
Pentacrythritol esters	Primarily used to formulate synthetic greases requiring excellent lubricating properties from -40°C to over 177°C
Polyglycols	These oils which tend to produce less carbonaceous residue upon degradation, find use in formulating greases for arcing electrical equipment.
Poly(α-olefins) (PAOs)	A relatively new class of synthetic hydrocarbon fluid available in a range of viscosities, these oils exhibit improved compatibility with ester-vulnerable thermoplastics and elastic
Polybutenes	A sunset of synthetic hydrocarbons with better viscosity-temperature characteristics than the PAOs and good properties as tackifier or damping fluid, but with a tendency to degrade under high shear.
Silicones	Outstanding thermo-oxidative stability, chemically inert, low and high temperature usefulness, and unmatched viscometric properties as a function of temperature. The viscosity index of one phenylsilicone is over 600.
Halocarbons	Chemically inert toward oxygen and possessing excellent innate boundary and extreme pressure lubricating properties, as well as extremely low temperature performance for the lighter viscosity grades.
Polyphenylethers (PPEs)	Two grades of these fluids are available, a five-ring and a six-ring molecule. The fluids possess exceptional radiation resistance, have outstanding thermo-oxidative stability and high surface energy, and have been used extensively for lubricating noble metal electrical contacts.

Table 2.2: Lubricating oils commonly used in synthetic greases (Continue) [6]

Fluids	Characteristic
Phosphate ester	Can be used to manufacture relatively in expensive greases that are able to resist ignition.
Perfluropolyethers (PFPEs)	Synthetic greases formulated from "branched" and "linear" versions of these fluids are inert toward oxygen and all but the most aggressive chemicals. Greases made from these oils have unsurpassed thermo-oxidative stability. The PFPEs with a straight polymer chain morphology ("linear PFPEs") also have excellent viscosity index and low temperature performance.
Multiply alkylated cyclopentances (MACs)	The newest commercially available synthetic fluid, demonstrating exceptionally low volatility under hard vacuum and elevated temperature.

Synthetic grease are prepared from both organic and inorganic thickeners. Organic thickeners are prepared from the reaction of a suitable alkaline metal with either high molecular weight carboxylic acids or fats. The alkaline metal are usually reacted with stearic acid, myristic acid, 12-hydroxy steric acid, or hydrogenated castor oil, a triglyceride that liberates 12- hydroxyl strearic acid doing saponification.

Inorganic thickeners, such as chemically modified clay, amorphous silica, and polytetrafluoroethylene, can also be used to form grease, but without the need for a chemical reaction for grease formation to occur. The efficiency of a particular thickener to convert synthetic oil into greases depends on the ultimate surface area of a thickener, its ability to bond with hydrogen. The thickener must have an affinity for the base fluid that is intermediate between the forces that lead to greater solubility and the forces rending to induce phase separation. This mesosolubility is a prerequisite for all successful grease formation.

2.3 Thickeners [6]

Thickeners are substances which, when added to an aqueous mixture it can increase its viscosity without substantially modifying its other properties they provide body, increase stability, and improve suspension of added ingredient .thickeners are not only transformed liquid lubricants into consistence lubricants. They also change the properties of the liquid lubricants. When or their properties are taken into consideration none of the commercially important thickeners stands out from any other as shown in Table 2.3. They are comparably competitive and suited for their tasks. The differences mainly lie in the more special demands made on them.

Table 2.3: Competitiveness of thickeners [6]

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Sur
Lithium 12-hydroxystearate	2.5	1.0	2.0	1.5	2.0	2.0	2.5	1.5	2.5	2.0	1.0	3.0	2.0
Calcium 12-hydroxystearate	3.0	1.0	3.0	1.0	1.5	1.0	2.5	1.0	2.0	2.0	1.0	3.0	1.8
Lithium complexes	1.5	2.0	1.5	2.0	1.5	2.0	2.0	2.5	1.5	2.0	2.0	2.5	1.9
	2.0	2.0	2.0	2.5	1.5	2.0	2.0	2.5	2.0	2.0	2.0	2.5	2.1
Aluminum complexes													
Calcium complexes	2.0	3.0	2.0	2.0	1.0	1.5	1.5	3.0	1.5	2.0	2.0	2.0	2.0
Inorganic thickeners	1.5	1.0	1.0	3.0	3.0	1.0	3.0	1.0	3.0	3.0	2.5	3.0	2.2
Polyureas	1.0	1.5	1.5	2.5	2.0	1.5	2.5	2.0	3.0	3.0	1.0	2.0	2.0
Terephthalamates	1.5	1.5	1.5	1.0	2.5	1.5	2.0	1.0	2.5	2.0	1.0	2.0	1.7
Calcium-sulfonate complexes	2.0	3.0	2.0	2.0	1.0	2.0	1.5	3.0	1.0	1.0	2.0	1.5	1.8
Carbamte-like thickeners	2.0	1.5	2.0	2.0	2.0	2.0	2.5	1.5	2.0	2.0	1.0	2.0	1.9

I = high temperature

II = low temperature

III = aging

IV = compatibility

V = oil loss

VI = toxicity

X = shear

XI = friction

XII = wear

1.0 = excellent

2.0 = average

3.0 = poor

Table 2.4: Thickeners commonly used in synthetic greases [6]

Gellants	Characteristic
Paraffin Wax	Low cost; low melting point
Alkali soap	Temperature to 200°C, pumpability, most common thickener
Organoclay	Temperature to 250°C, high loads, incompatible with some polar additives
Alkali complex soap	Temperature to 250°C, pumpability, water resistance
Polyurea	Temperature to 250°C, pumpability, stability, excellent in high load bearing
PTFE	Temperature to 300°C, low coefficient of friction, inert, moderate load only
Silica	Nonmelting, water resistance, low oil separation/good oil retention
Metal oxide	Nonmelting, thermal conductivity, inert

Table 2.5: Alkali metals used to prepare alkali soap thickener greases [6]

Alkali	Formula
Lithium hydroxide monohydrate	$LiOH \cdot H_2O$
Calcium hydroxide	$Ca(OH)_2$
Sodium hydroxide	$NaOH$
Aluminum hydroxide	$Al(OH)_3$

2.3.1 Simple soaps

In general, a maximum thickening effect is achieved with carboxylic acid s having 18 carbon atoms. Soaps are usually prepared from vegetable-derived 12-hydroxylstearic acid or from animal or vegetable-derived stearic acid, or from their esters, usually their glycerides, and from the hydroxides of elements of the alkali and alkaline earth metals. Soaps, by gelling their base oils give grease most of their unique properties. They are not only present as crystallites and dissolved molecule, but above all in a separate phase represented by agglomerate called fibrils or fibers. All components are presented, and have the properties of grease, even in the smallest lubrication gap.

2.3.2 Soap Anions

The carbon chain length of a carboxylic acid affects the solubility and surface properties of soap. Longer and shorter carbon chains reduce its thickening capacity. Increasing the chain length increases the solubility in the base oil, shortening the chain length reduces it. A branched alkyl chain lowers the melting point of soap and reduces its thickening effect. Carboxylic acids containing carbon double bonds, so called unsaturated acids, are more soluble in mineral oils and also reduce the thickening effect and lower the dropping point. Their use is limited because of their lower oxidation stability. Hydroxyl groups increase the melting point and the thickening effect of soap because of its increased polarity.

2.3.3 Soap Cations

The soap cations also are responsible for essential properties of soap greases. The cations govern the thickener yield, the dropping point, according to DIN ISO 2176 the temperature at which a grease gets liquid under normal conditions, the resistance, and to some extent, the load-carrying capacity of a greases.

2.3.4 Lithium Soaps

Nowadays Lithium soap-based greases are usually prepared by reacting lithium hydroxide as a powder or dissolved in water with 12-hydroxystearic acid or its glyceride in mineral oils or synthetic oils. Whether the free acid or its glyceride is preferred depends on the relationship between cost and performance. The production temperature is between 160 and 250°C, depending on the base oil and the type of reactor in use. The dropping point of mineral oil-based NLGI 2 grease is usually between 185 and 195°C. For such a multi-purpose grease ca 6% w/w of soap is required with a naphthenic oil, ca 9% w/w with paraffinic oil, and ca 12% w/w with a polyalphaolefin, and a kinematic viscosity of ca 100 mm^2s^{-1} at 40°C (the thickening effect depends not only on the carbon distribution in a base oil, but also on its viscosity).

The fiber size in lithium 12-hydroxystearate greases is usually between 0.2 x 2 and 0.2 x 20 µm. Good multi-purpose properties, e.g. a high dropping point, good water resistance, good shear stability – which has been related to hydrogen-bonding of the hydroxyl groups – and good response to additives are the reasons why lithium 12-hidroxystearate-based greases have now been the most popular for more than half a century. They have found a wide range of applications from extreme-pressure (EP) greases based on oils with kinematic viscosities of ca 200 to 1000 mm^2s^{-1} at 40°C for heavy loads, through multi-purpose greases based on mineral oils with kinematic viscosities from 60 to 120 mm^2s^{-1} at 40°C for all kinds of bearings; greases made with diesters or polyalphaolefin oils and kinematic viscosities of 15 to 30 mm^2s^{-1} for high-speeds, to those with oil-insoluble polyalkyleneglycols for gears. The lower application temperature limit for lithium soap thickened grease, as for all other greases, depends mainly on the physical properties of its base oil, of course. The upper limit is depending on the base oil, it lies between 120 and 150°C. It is readily apparent that between the dropping point and the upper application temperature limit there can be a gap of between 60 and 100°C. Oil separation has been discussed as a criterion for both lower and upper application temperature limits.

2.3.5 Calcium Soaps

Calcium soaps prepared from 12-hydroxystearic acid, called anhydrous calcium soaps. Similar to the corresponding lithium soaps they indeed contain up to 0.1% w/w, but that water is not present as a crystallization component, as in stearic acid based soaps, although technical 12-hudroxystearates contain up to 15% w/w stearic acid. Calcium greases of this type are produced in the same way as lithium soap-based greases, but at temperature between 120 and 160°C. The size of their fibers lies between those for lithium soaps and hydrated calcium soaps. The greases can be used up to 120°C. Their dropping point is between 130 and 150°C, depending on their base oil. They usually have a very good corrosion resistance and good oxidation stability; when prepared from suitable base oils they are possibly the best low-temperature greases.

Calcium soaps mainly based on stearic, palmitic, or oleic acid still are called hydrated calcium soaps. For these greases the cost of raw materials, and the performance levels, are lowest. They are prepared by neutralization of slurry of calcium hydroxide in water with fatty acids or fats in mineral oil. Fats are cleaved in the first reaction step into fatty acids and glycerol. This is usually performed in a pressure vessel. Stable greases can only be obtained in the presence of some water, usually ca 10% w/w of the soap. The water content is usually adjusted in a second step in a stirring, or cooling vessel. When the water is removed, the grease structure collapses. The dropping point of this type of grease is therefore only 90 to 110°C and the upper application temperature limit is only ca 80°C.

The greases have very good water resistance and good adhesive properties. Because their manufacture is rather demanding in relation to the performance obtained, their importance is declining rapidly.

2.3.6 Sodium soaps

Compared with lithium and calcium 12-hydroxystearate greases the importance of greases based on sodium soaps is nowadays low, although in the form of semi-fluid products they still are of some interest for the lubrication of gears. Sodium greases made from fatty acids or fats have dropping points of Ca 165 to 175°C. The upper temperature limit is Ca 120°C. Products are available with short and long fiber structures; the latter reaching up to 1x 100 μm and are responsible to some extent for the rather high load carrying capability in gears. Although the greases have extraordinary good corrosion- preventive properties if only small amounts of water are present, their main disadvantage is the solubility of the sodium soaps in larger amounts of water; this leads first to gel formation, which dramatically increased the apparent viscosity, and later to breakdown of the whole structure.

2.3.7 Other Soaps

Aluminum soap-based greases are usually produced with pre-manufactured aluminum soaps, usually aluminum stearate. They have dropping points of up to 120°C, their upper temperature limit is 80 to 90°C they tend to gel. Typical of this soap is a particle size of less than 0.1 x 0.1 μm, which is to some extent responsible for the low shear stability and the pronounced thixotropic behavior of the products. Aluminum greases are usually very transparent and smooth. They have good water resistance and adhesive properties, but have been widely replaced by lithium greases, partly because, for consistent products, aluminum greases must not be stirred during the finishing process but poured into pans and left for several hours to cool.

Barium soap-based greases have high water resistance and shear stability, and lead soap-based greases have advantageous load-carrying capacity and wear protection properties. Both have, nevertheless, been completely been replaced, mainly for toxicological reasons.

Lithium-calcium greases have become quite popular as specialized multi-purpose greases. Greases mainly based on sodium-aluminum stearate, have been used as substitutes for lithium greases, for example in the former GDR. Cation mixed soap greases are usually manufactured by a one-step process, because the stability of mixtures of finished products are not always satisfactory.

2.4 Base oil [6]

Base oil is the main component of lubricant blends. In general only oils with kinematic viscosities from 15 to 1500 mm^2 at 40°C are used. The oils with the lowest viscosities and the best low – temperature properties have the lowest operational temperatures at the highest speeds the oils with the highest viscosities have the best performance at the lowest speeds and the highest loads, the lowest evaporation loss, the strongest adhesion and the best water or solvent resistance.

2.4.1 Mineral oils

Oils with low viscosity index (VIs) usually require less thickener than those with high VIs and the same kinematic viscosity. The latter can be used over a wider temperature range. In principle the thickening effect (yield) depends on the difference between the solubility parameters of the base oil and thickener. Because oil separation depends on the concentration of thickener, at a given temperature oil separation is most pronounced for greases based on low VI oils .e.g. aromatic oils or alkyl-benzenes .oil separation goes though a minimum with increasing kinematic viscosity for a given kind of base oil. This can easily be understood when only the dependence of particle interactions on the size of the involved particles is considered. Some of the specific properties of greases also depend on the ratio of the temperature and the pressure coefficients of the viscosity of their base oils. If all this is taken into account, the effect of even a small change in base oil composition on the performance of grease should not be underestimated.

2.4.2 Synthetic base oils

Synthetic oils are used in greases only when the performance required cannot be achieved with mineral oils. Even today greases of this kind represent less than 5% of overall grease consumption.

2.4.2.1 Synthetic Hydrocarbons

Poly(α- olefins) is the ideal base oils for wide temperature-range greases. They are usually used in the same viscosity range as their mineral oil equivalents, but whereas the upper kinematic viscosity border of the former is ca 50 mm^2s^{-1} at 100°C, Poly(α- olefins) and similar products are available to ca 2000 mm^2s^{-1} at 100°C. In contrast with mineral oils they are preferably shrinking rather than swelling polymeric sealing materials. Therefore, esters with softener properties must be added. Greases made from Poly(α- olefins) with standard viscosities are usually meant for lifetime lubrication, those made from mixtures with mineral oils are often called semi-synthetic and are used in specialized greases to increase lifetime.

2.4.2.2 Other Synthetic Base Oils

High molecular-weight esters made from diols or polyols and dicarboxylic acids with viscosities greater than 2000 mm^2s^{-1} at 40°C are used as base oils in greases that must be solvent resistant.

Silicone oils can be regarded as polyethers of alkylated silicic acids. In contrast with other greases silicone greases are better distinguished according to the properties of their base oils. The kinematic viscosities of silicone oils for greases range from ca 75 to ca 1000 mm^2s^{-1} at 40°C. Dimethylsilicone oils are physiologically inert; when thickened which highly dispersed silicic acid they are mainly used as sealants or in applications where specific electrical and thermal conductivity is important.

Apart from being suitable for temperature up to 270°C perfluorinated ethers thickened with PTFE powders are the only greases that can work in the presence of aggressive chemicals such as oxygen or chlorine. This is also their main advantages over the corresponding greases based on partially fluorinate silicone oils.

2.4.2.3 Immiscible Base Oil Mixtures

Greases are the only lubricants that with their thickeners have brackets at their disposal to force immiscible liquid component into one lubricant. Friction of hydrocarbon or ester-based greases can be reduced in this way and lifetime can be prolonged with polyethers and with polyester. Similar results have been reported for greases made from Poly (α - olefins) and perfluorinated ethers.

2.5 Additives [6,7]

Most of the additives used in liquid lubricants can be used in greases, although in general at clearly higher concentration as shown in Table 2.6. Interactions of thickeners and additives must therefore always be considered.

Table2.6: Usual grease additive levels (%) [7]

Additives	% wt. in grease
Antioxidants	0.10 – 1.00
Corrosion inhibitors	0.50 – 3.00
EP/AW additives	0.50 – 5.00
Metal deactivators	0.05 – 0.10
Solid lubricants (black)	1.50 – 3.00
Tackifiers	0.10 – 1.00

EP (extreme pressure) is the additive for lubricants with a role to decrease wear of the parts of the gears exposed to very high pressures. EP typically conyains organic sulfur, phosphorous or chlorine compound including sulfur-phosphorous and sulfur-phosphorous-boron compound, which chemically react with the metal surface under high pressure condition. AW is the anti-wear additives to prevent metal to metal contact between parts of gears. AW typically contains zinc and phosphorous compound.

A typical lithium 12-hydroxystearate-based multi-purpose grease contain at least 0.2% w/w of an antioxidant or a mixture of antioxidants, between 0.5 and 1.0% w/w of one or several corrosion inhibitors, ca 0.05% w/w of a metal deactivator and (in its EP-version up to 2.5% w/w EP/AW additives) depending on the type chosen:

2.6 Manufacture of greases [6]

The properties of greases, especially metal soap-based greases, depend not only on their composition but also, and to nearly the same extent, on the way in which the thickeners are prepared and dispersed.

2.6.1 Metal Soap-Based Greases

2.6.1.1 Batch Production with Preformed Metal Soaps

It is possible, as one stage of grease manufacture, for a metal soap prepared in an independent first step, or a commercially available soap, to be dissolved or dispersed and heated and cooled again under defined conditions in suitable base oil. But because of the higher costs of the thickeners this method can be recommended only for highly sophisticated synthetic greases with precise chemistry or for functional base fluids that would react with the water or, even worse, with the steam generated during neutralization process.

2.6.1.2 Batch Production with Metal Soaps Prepared In-situ

In general fatty acids or their glycerides or even their methyl esters are reacted with aqueous solutions or suspensions of the described metal hydroxides in part of the base oil. Each batch of grease is produced by following a ten-point schedule as shown in Table 2.7

When base oils such as silicone oils used for the in-situ production of soap greases, the thickeners are sometimes formed and dispersed in the presence of solvents which are subsequently removed by extraction or evaporation.

The batch production of metal soap greases can be automated. This has been achieved with the aid of value engineering and computer control.

Table 2.7: Batch production of soap based greases – ten point schedules. [6]

Schedule	Instructions
1	Dissolution of dispersion of the fatty acids in one third to two thirds of the base oil at temperature up to 90°C;
2	Addition of the metal hydroxides as a solution or suspension in water,
3	Heading to temperature between 115 to 150°C or under pressure at 180 to 250°C depending on the type of reactor,
4	Dehydration of the soap by heating to 80 to 200°C or by pressure release;
5	Crystallization during cooling to 150 to 130°C combined with addition of more base oil;
6	Addition of additives at temperatures below 80°C;
7	(pre)filtration and homogenization with one of several possible devices;
8	Adjustment of the specified consistency or flow pressure;
9	(end)filtration and deaeration; and
10	Packing into containers

2.6.1.3 Continuous Production

The advantages of such a unit are its compact size (a few hundred liters only), its minimal energy consumption, and the uniformity of the product; the disadvantages are the difficulty of producing different ranges of products and the capacity of such units - far bigger than the need for common greases nowadays. Continuous production of highly sophisticated greases has not been possible for many years, but recently the continuous manufacture of lithium complex greases has been reported.

Comparison of the different processes used to make metal soap-based greases shows that no single process is optimum for every kind of grease and investigation of four processing system for lithium greases, including high concentrate saponification, indicates that manufacturing greases by conventional methods is not necessarily a disadvantage.

2.7 Grease Performance [6]

The performance of grease is, again, probably best judged in terms of the thickener. From a more theoretical view there are twelve main phenomena which must be considered. Of these twelve, all but two – tackiness and toxicity – are related either to pressure or to temperature. The action or effect of pressure or temperature results in twenty-four requirements (Table 2.8). It is out of question for a real grease to satisfy all these requirements. Because there are eleven necessary performance contradictions and thirty-three more or less marked restrictions. The suitability of grease for both high- and low-temperature applications is, difficult to achieve, although the lower and upper temperature limits of grease exceed those of its base oil, by analogy with Raoult's law. This means that the thickener acts as an impurity that, on the one hand, hinders crystallization and thus lowers the pour-point of the oil yet, on the other hand, reduces its vapor pressure. The effect can be increased by using of the kind of polymer employed as pour-point depressants and viscosity index improves in lubricating oils. The temperature-dependence of the apparent viscosity of grease – at constant shear rates – is less pronounced than that of its base oil.

Table 2.8: Twenty-four properties of greases [6]

Twelve phenomena	Twenty-four properties
High temperature	Maximum thermal stability
	Minimum evaporation loss
	Maximum viscosity
Low temperature	No (regular) crystallization
	Minimum viscosity
Aging	Maximum oxidation resistance
	Resistance to changes in structure
Compatibility	No reaction with non-ferrous metals
	Maximum corrosion inhibition
	Maximum polymer compatibility
	Immiscibility with foreign liquids
	Deflection of foreign solid matter
Oil loss	Optimum oil loss [a)]
Toxicity	No toxicity
	Biodegradability
Tackiness	Optimum tackiness [a)]
Flowability	Optimum relaxation [a)]
	Maximum pumpability [a)]
Shear	Maximum mechanical stability, or
	Optimum relaxation time [a)]
Load	Optimum elasticity [a)]
	Maximum lubricating film thickness
	Maximum emergency running properties
Friction	Minimum, or optimum friction [a)]
Wear	Minimum wear

[a)] According to application

Sometimes, usually when a unit is lubricated with a new grease, the performance of the second grease can be affected by the first. Cleaning of the unit is, therefore, always the best solution. The danged resulting from mixing two greases is nevertheless often overestimated and some of the charts describing incompatibilities in the grease literature are seen contradictory. Possible incompatibility is the best checked experimentally with the so-called Shell-roller test. A change in the structure usually leads to softening of the mixture and to a decrease of the dropping point. Mention is to make of two incompatibilities only – that between lithium and sodium soap-based greases and that between inorganic thickened greases and other greases with many additives. Both occur in practical grease lubrication and are caused by the thickeners. Loss in performance otherwise is simply because of the lower efficiency of the first grease. If the greases contain very different and reactive additives this can also result in incompatibility.

2.8 Applications of Greases [6]

Increased knowledge of base oils and thickener systems enables the selection and naming of greases on the basis of these chemical and physical insights. The selection of grease is always a compromise between the demands of a customer and the circumstances the grease must face during its operational life – temperature, speed, load including centrifugal forces and vibrations, re-lubrication intervals based on a knowledge of the lubrication points, for applications which can be roller bearings, plain bearings, classis, joints, 5th wheels, door locks, switches and seals of different design.

2.9 Test Methods for Grease [6-8]

Many test methods are used today; all are meant to judge the single or combined and more or less complex properties of greases. The last summary containing detailed descriptions of ASTM and DIN methods was written by Schultze in 1962; another emphasizing on Russian GOST and former East German TGL methods was published in 1984. The most important ASTM and DIN methods are described in Table 2.9 and 2.10. Complete collections are published regularly; the same is true for the French AFNOR, the English IP, the Japanese JIS, and some other national collections. The development of international standards (EN and ISO) is slowly proceeding.

Because of the large number of publications about the different test methods, their improvement, and their comparison, few surveys concerned with EP, wear and with standard tests or performance tests using real components are cited. There are also at least two new test methods that might be helpful in the future, the tipping rod method for determination of the yield point of semi-fluid greases and the Vogel-Marawe test device for determination of oil separation under pressure and which enables the observation of hardening tendencies simultaneously.

Table 2.9: Important ASTM test methods for lubricating greases. [6]

Test Method	Properties
ASTM D 1092-93	Apparent viscosity
ASTM D 1263-94	Leakage tendencies of automotive wheel bearing greases
ASTM D 1264-96	Water washout characteristics
ASTM D 1478-91	Low-temperature torque of ball bearing greases
ASTM D 1742-88	Oil separation during storage (air pressure method)
ASTM D 1743-94	Corrosion preventive properties
ASTM D 1831-88	Roll stability
ASTM D 2509-93	Load carrying capacity, Timken method
ASTM D 3337-94	Life and torque in small bearings
ASTM D 2265-06	Dropping point of lubricating grease over wide temperature range
ASTM D 217-97	Cone Penetration of lubrication grease

Table 2.10: Important DIN (ASTM) test methods for lubricating greases [6]

Test Method	Descriptions
DIN 51350-4 (ASTM D 2596-97)	Testing in the Shell four-ball tester, determination of the welding load of consistent lubricants
DIN 51350-5 (ASTM D 2266-91)	Testing in the Shell four-ball tester, determination of the wear parameters of consistent lubricants
DIN 51801 (ASTM D 566-97, replaced by DIN ISO 2176)	Determination of dropping point of greases
DIN 51802	Testing of rolling bearing greases with regard to their corrosion-inhibiting properties, SKF-Emcor method
DIN 51804-1 (ASTM D 217-97), replaced by DIN ISO 2137)	Determination of cone penetration of greases with hollow cone and solid cone
DIN 51804-2 (ASTM D 1403-97), replaced by DIN ISO 2137)	Determination of cone penetration of greases with one-quarter cone
DIN 51805	Determination of yield pressure of lubricating greases, Kesternich-method
DIN 51807-1	Test for the behavior of grease in the presence of water, static test
DIN 51808 (ASTM D 942-90)	Determination of oxidation stability of greases, oxygen method
DIN 51810	Determination of flow behavior of greases in the rotary viscometer
DIN 51811 (ASTM D 4048-86)	Testing of corrosive effects of greases on copper, copper strip test
DIN 51817	Determination of oil separation from greases under static conditions
DIN 51821-2	Test using the FAG roller bearing grease testing apparatus FE 9

2.10 Literature reviews [4,5,9,10]

D. Ratanaleart, P. Chotikarnruengchai, F. Pintanonda, and V. Chuenchom studied the percentage of grease from glycerol, fatty acids, and used cooking oil. The grease formulation was prepared from base oil and thickener. Base oil was synthesized from the esterification between glycerol and oleic acid by 1 to 1 mol ratio at 100°C for 3 days followed by the esterification with adipic acid by 1 to 1 mol ratio at 140°C for 3 days. The thickener was synthesized as solid ester from the esterification reaction between glycerol and palmitic acid by 1 to 1 mol ratio at 100°C for 5 days followed by the esterification with adipic acid by 1 to 1 mol at 140°C for 7 days. Soap was made from the saponification of used cooking oil. Three sample of grease were formulated by using the oil/thickener ratios from 90:10 to 80:20, and 70:30. The grease with 90 to 10 ratio was not thick enough. The other grease samples were subjected to the dropping point testing. It was found that the dropping point of grease with 80:20 and 70:30 ratio were 94°C and 77°C. The grease sample with 80:20 ratio which had higher dropping point was tested for water wash out to find the percentage of weight loss at 38°C. It was found that 92% weight was lost. The results showed that the product from this work were not suitable for use in industrial application.

Synthesis and properties of 9,10-epoxystearic acid derivatives with various alcohols was studied by T. Wattanakul and V. Chuenchom. The conversion of oleic acid, the model compound representing unsaturated fatty acids in vegetable oils, to 9,10-epoxystearic acid via epoxidation with peracetic acid using sulfuric acid as catalyst was determined. The suitable epoxidation condition was investigated by the variation of hydrogen peroxide, acetic acid and sulfuric acid content, reaction time, and reaction temperature. Moreover, two synthetic procedures, namely two-step synthesis (a generation of peracetic acid prior to epoxidation) and single-step synthesis (a generation of peracetic acid during epoxidation) were compared. It was found that the two-step synthesis provided a relatively higher conversion of oleic acid and higher yield of epoxidised product, as compared to the single-step synthesis. In addition, water and acetic acid in the presence of high H_2SO_4 content produced the by-products, namely diol and hydroxyl-acetoxy compounds, from the ring-opening of epoxidised product. Experimental results showed that 76%

conversion of oleic acid and 70.64% yield of epoxidised product were obtained by using 0.6 mol of hydrogen peroxide, 0.2 mol of acetic acid, 0.1 mol of oleic acid and 0.007 mol of H_2SO_4. The optimized reaction temperature for peracetic acid preparation and for epoxidation was 50°C and 30°C whereas the optimized reaction time for peracetic acid preparation and for epoxidation was 4 and 15 hours, respectively.

Vaibhav V. Goud1, Anand V. Patwardhan, Srikanta Dinda, and Narayan C. Pradhan studied the epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. The kinetics of epoxidation of jatropha oil by peroxyacetic/peroxyformic acid, formed *in situ* by the reaction of aqueous hydrogen peroxide and acetic/formic acid, in the presence of an acidic ion exchange resin as catalyst in or without toluene, was studied. The presence of an inert solvent in the reaction mixture appeared to stabilise the epoxidation product and minimise the side reaction such as the opening of the oxirane ring. The effect of several reaction parameters such as stirring speed, hydrogen peroxide-to-ethylenic unsaturation molar ratio, acetic/formic acid-to-ethylenic unsaturation molar ratio, temperature, and catalyst loading on the epoxidation rate as well as on the oxirane ring stability and iodine value of the epoxidised jatropha oil were examined. The multiphase process consisted of a consecutive reaction, acidic ion exchange resin catalysed peroxyacid formation followed by epoxidation. The catalytic reaction of peroxyacetic/peroxyformic acid formation was found to be characterised by adsorption of only acetic (or formic) acid and peroxyacetic/peroxyformic acid on the active catalyst sites, and the irreversible surface reaction was the overall rate determining step. The proposed kinetic model took into consideration of two side reactions, namely, epoxy ring opening involving the formation of hydroxy acetate and hydroxyl groups and the reaction of the peroxyacid and epoxy group. The kinetic and adsorption constants of the rate equations were estimated by the best fit using nonlinear regression method. Good agreement between experimental and predicted data validated the proposed kinetic model. From the estimated kinetic constants, the apparent activation energy for epoxidation reaction was found to be 53.6 kJ/mol. The value compared well with those reported by other investigators for the same reaction over similar catalysts.

The synthesis of biodiesel and lubricants from purging nut oil was researched by J. Thongmool and V. Chuenchom. Purging nut oil, which had a triglyceride structure, was changed into a monoester structure by transesterification reactions with six alcohols which were methanol, ethanol, 1-butanol, 1-hexanol, 1-octanol, and 1-decanol respectively, in the presence of concentrated sulfuric acid and sodium methoxide as catalyst. It was found that, with an increase in the mole ratio of alcohol/oil, the amount of catalyst, reaction temperature and reaction time, the reaction rate was raised and gave the higher percent yield of ester products. Moreover, that base catalyst was shown to be more effective than acid catalyst as the same amount of catalyst was used.

Chapter 3

Experimental details

3.1 Chemical and materials

1. Conc. H_2SO_4: Baker Analyzed, LOT: G10W62
2. Sodium Hydroxide: Lab-scan analytical sciences, Code no.:K2001
3. 98 % Acetic acid: Glacial, Baker Analyzed, LOT : J51T01
4. 30 % Hydrogen peroxide: Carlo Erba Reactifs, Batch Number V1I768161I
5. Diethyl ether: Carlo Erba Reactifs, Batch Number 0F715200G
6. Plamitic oil: Oleen Brand

3.2 Equipments and instruments

1. Magnetic bar
2. Heater with thermostat: IKA, model: C-MAG HS7
3. Beaker: 250 ml and 100 ml
4. Round-bottom flask: 250 ml and 100 ml
5. Oil bath
6. Distillation apparatus
7. Aluminum foil
8. Graduated cylinder
9. Nuclear Magnetic Resonance (NMR): Bruker, Model: Avance DPX 300

10. Blender: PHILIPS, MODEL: HR2001 5 stars blade and 350w motor

11. Dropping point apparatus: Petrotest, Model: Jumotron

12. Water washout apparatus: Stanhope seta, Model: 19610-4

3.3 Synthesis of ester product from castor oil

1. 85.23 g of 30% of hydrogen peroxide (0.75 mole), 12.27 g of 98% acetic acid (0.2 mole), and 0.4 mL of sulfuric acid (0.008 mole) were added into a 250 mL round bottom flask equipped with a magnetic bar.
2. Place the flask in a paraffin oil bath. The system was kept at 50°C and the mixture was continuously stirred for 4 hours.
3. The mixture was cooled down to room temperature and 29.71 g (0.1 mole/ double bond mole) of castor oil was gradually added.
4. After the charging of castor oil was completed, the reaction continued by stirring for 15 hours at room temperature.
5. The product was separated and analyzed by ^{1}H NMR technique.
6. Step 1 to 5 were repeated by changing the variables as shown in table 3.1.

Table 3.1 conditions used in the synthesis of ester product from castor oil

Batch	Castor oil (mole)	H_2O_2 (mole)	CH_3COOH (mole)	H_2SO_4 (mole)
1	0.1	0.75	0.20	0.008
2	0.1	1.5	0.40	0.016
3	0.1	2.78	0.74	0.030

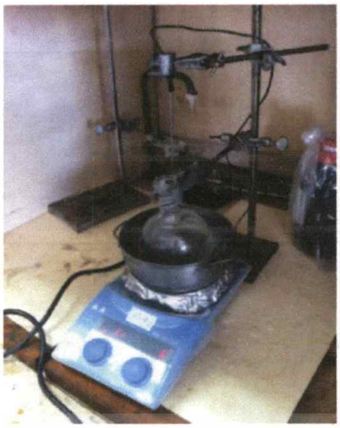


Figure 3.1 Apparatus for synthesis of ester product from castor oil

3.4 Soap preparation

1. 4.9 g of sodium hydroxide was mixed with 10 mL of water in a 50 mL beaker.
2. Sodium hydroxide was stirred until completely dissolved into 12.25 M NaOH.
3. 20 mL of palm oil was placed in a 100 mL beaker.
4. 12.25 molar of NaOH solution was added from above dropwise while heating and stirring at 70 °C until the mixture became solid.

3.5 Grease preparation

1. 90 g. of synthesized base oil from part 3.3 was added to 10 g of soap mixture from part 3.4.
2. The mixture was blended by blender for 30 minutes until it became smooth cream.
3. Previous steps were repeated by changing the amount of base oil to soap from 90:10 to 80:20, 70:30, and 60:40, respectively.

3.6 Dropping point testing by ASTM D 2265 [12]

Figure 3.2 Dropping point apparatus

1. Insert empty test tubes in every test tube well and a thermometer having a range from -5 to 400 °C in the thermometer well of the oven.
2. Turn on the oven and select the lowest aluminum block oven temperature setting from the four listed below that will result in an observed dropping point at or below the corresponding maximum observed dropping point show for that oven temperature setting.
3. Select and use test tubes and accessories to minimize wobble of the thermometer. All components must be at room temperature prior to the test. Place the components through on the thermometer. Adjust the bushing and the bushing support ring so that is about 25 mm from tip of the thermometer. Place the cup support in tube. Insert the thermometer depth gage and the thermometer assembly in the tube. Position the thermometer so that the tip bottoms in the gage. Adjust the bushing and thermometer clamp so that the bushing shoulders on the top edge of the tube.
4. Select a clean cup, and fill it with grease either by punching the cup into the sample presented or by using a small spatula. Overfill the cup, and use the spatula to force some of the grease out of the bottom hole of the cup to help remove any trapped air. Add more samples and strike off the excess grease level with the top of the cup. Gently press the cup, held in a vertical position with the smaller opening at the bottom, down over the

metal rod until the latter protrudes about 25 mm. Press the rod against the cup in such a manner that the rod makes contact at both the upper and lower peripheries of the cup. Maintain this contact, rotating the cup on the rod along the index finger to give it a spiral like motion down the rod to remove a conical section of the grease which adheres along the rod. As the cup approaches the end of the rod, carefully slip the rod out of the cup, without marring the inside surface of the grease, so that a smooth film of reproducible thickness remain inside the cup. If surface has been touched by the rod or any air bubbles are noted, repack the cup

5. Remove the thermometer assembly and depth gage from the tube. Place the grease cup on the cup support in the test tube and carefully reinsert the thermometer assembly. Make no further adjustment as the thermometer assembly. Make no further adjustment as the thermometer bulb is now positioned to provide adequate clearance between the tip of bulb and grease sample in the cup.
6. After making certain that the oven temperature has stabilized, remove an empty tube from the oven and gently insert the tube assembly in its place. Exercise care to ensure that the cup remains upright in the cup support. If the cup is tilted, the thermometer bulb can come in contact with the film of grease and result in an erroneous value.
7. When the first drop of material falls free of the cup orifice and reaches the bottom of the test tube, record both the temperature of the cup and of the oven to the nearest degree. Certain grease, for example, some simple soap compositions, or those containing some types of polymers can form a drop with a tailing thread which can hold until the drop reaches the bottom of the test tube is recorded as the observed dropping point.

3.7 Cone penetration testing by ASTM D 217-97 [13]

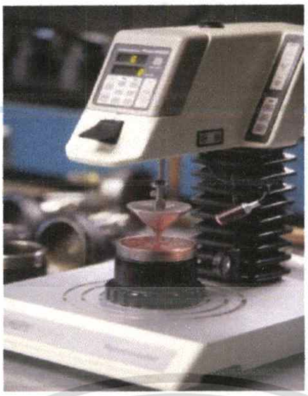


Figure 3.3 Apparatus for cone penetration of lubricating grease

1. Place the cup on the penetrometer table, making certain that it cannot teeter.
2. Set the mechanism to hold the cone in the zero position, and adjust the apparatus carefully so that the tip of the cone just touches the surface at the center of the test specimen.
3. Watching the shadow of the cone tip, from a low angle with backlighting, is an aid to accurate setting. For greases with penetrations over 400, the cup must be centered to within 0.3 mm (0.01 in.) of the tip of the cone. One way to center the cup accurately is to use a centering device.
4. Release the cone shaft rapidly, and allow it to drop for 5.0 6 0.1 s. The release mechanism should not drag on the shaft. Lock the shaft in position at the end of the 5-s period. Gently depress the indicator shaft until stopped by the cone shaft and read the penetration from the indicator.

Chapter 4

Results and discussion

Grease generally contains base oil and thickener. The purpose of this research was to formulate grease from a derivative of epoxidised castor oil and sodium soap from palm oil. The preparation of base oil was attempted from the esterification reaction of castor oil with peracetic acid prepared from H_2O_2 and acetic acid as explained in Chapter 3.

4.1 Synthesis of epoxidised castor oil (ECO), its derivatives and their characterization

From the research done by T. Wattanakul and V. Chuenchom, the synthesis of 9,10-epoxystearic acid by epoxidation of 0.1 mole of oleic acid with peracetic acid generated from 0.75 mol of hydrogen peroxide and 0.2 mol of acetic acid in the presence of 7.5×10^{-4} mol of sulfuric acid catalyst showed 76 % conversion of oleic acid as the highest. The optimized reaction temperature for peracetic acid preparation and for epoxidation was 50 °C and 30 °C whereas the optimized reaction time for peracetic acid preparation and for epoxidation was 4 and 15 hours, respectively. The use of n-decanol to open the epoxy rings showed 86.88 % conversion. The remaining rings were consecutively opened by acetic acid and water presented in the reaction mixture. This led to the variety of products which were difficult to identify and characterize. In this work, many attempts were carried out to completely epoxidise the double bonds of castor oil and to get high selectivity towards one product. A structure of castor oil and its ^{1}H-NMR spectrum were shown in Figure 4.1 and 4.2, respectively. A structure of epoxidised castor oil with epoxide rings partially-opened by acetic acid and water is illustrated in figure 4.3. The important signals and their chemical shifts from ^{1}H-NMR spectra of castor oil, epoxidised castor oil and its derivatives from this work were shown in Table 4.1.

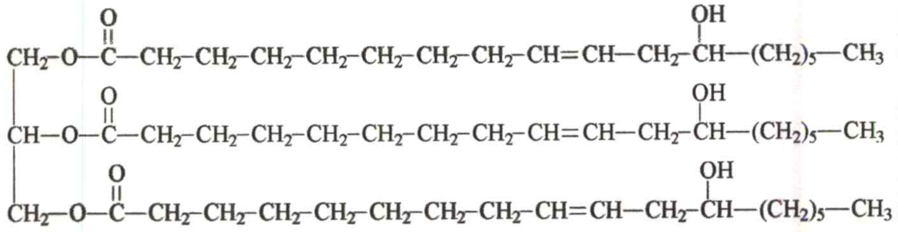


Figure 4.1 A structure of castor oil

Figure 4.2 The ^{1}H-NMR spectrum of pure castor oil

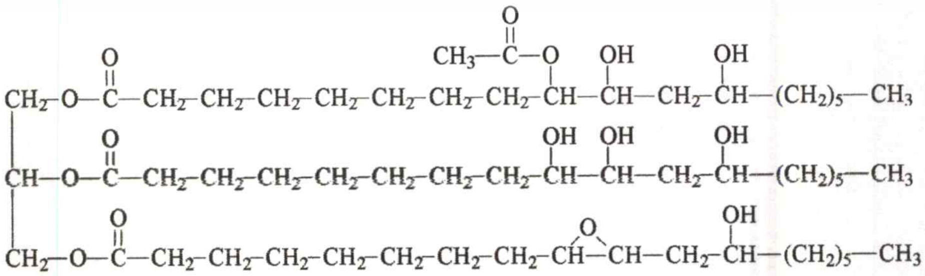


Figure 4.3 A structure of epoxidised castor oil with epoxide ring partially-opened by acetic acid and water

Table 4.1 The signals from ^{1}H-NMR spectrum of castor oil, epoxidised castor oil (ECO), and ECO derivatives.

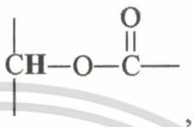
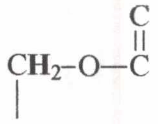
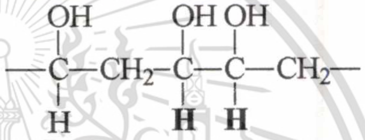
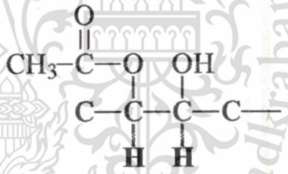
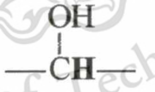
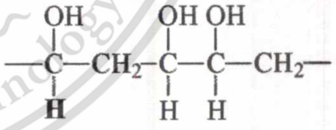
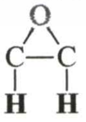
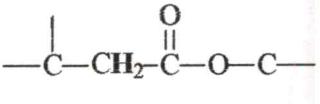
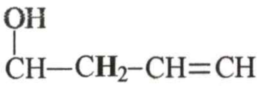
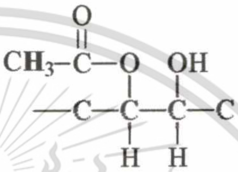
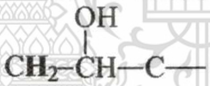
δ (ppm)	Signals
5.2-5.8	**$HC{=}CH$** (1)
5.2	**—OH** (2)
4.0-4.4	 $-\underset{\vert}{\overset{\vert}{C}}H-O-\overset{O}{\overset{\Vert}{C}}-$,  $\underset{\vert}{CH_2}-O-\overset{C}{\overset{\Vert}{C}}$ (3) (4)
3.5-4.0	 $-\underset{H}{\overset{OH}{C}}-CH_2-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-CH_2-$, (5)  $C-\underset{H}{\overset{O-\overset{O}{\overset{\Vert}{C}}-CH_3}{C}}-\underset{H}{\overset{OH}{C}}-C-$ (6)
3.3-3.6	 $-\overset{OH}{CH}-$,  $-\underset{H}{\overset{OH}{C}}-CH_2-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-CH_2-$, (7) (8)
2.9-3.2	 $\overset{O}{\underset{H}{C}-\underset{H}{C}}$ (9)
2.2-2.4	 $-\overset{\vert}{C}-CH_2-\overset{O}{\overset{\Vert}{C}}-O-C-$ (10)

Table 4.1 The signals from ^{1}H-NMR spectrum of castor oil, epoxidised castor oil (ECO), and ECO derivatives. (Continued)

δ (ppm)	Signals
2.1-2.2	 $\overset{OH}{CH}-CH_2-CH=CH$ (11)
1.9-2.1	$CH_2-HC=CH$ (12)  (13)
1.5-1.7	 $-CH_2-C-\overset{O}{\overset{\|}{C}}-O-C$ (14)
1.3-1.5	 $CH_2-\overset{OH}{CH}-C-$ (15)
1.1-1.3	$CH_2-CH_2-CH_2$ (16)
0.8-1.0	CH_3-R (17)

The first attempt started with the use of 0.1 mole of castor oil reacted with peracetic acid generated from 2.78 mol of hydrogen peroxide and 0.74 mol of acetic acid in the presence of 0.03 mol of sulfuric acid catalyst (Batch 3, Table 3.1). The amount of reagents used here was more than that used in the research done by T. Wattanakul and V.Chuenchom as an attempt to completely oxidise the double bonds. The signals from ^{1}H-NMR spectrum of the product (Table 4.1) showed the disappearance of double bonds, at δ 5.2-5.8 ppm (signal (1), Table 4.1) as expected. However, the signals at δ 2.9 – 3.2 ppm which was those of epoxidised ring (signal (9)) were not present. This can be explained by the appearances of signals at δ 1.9-2.1 ppm (signal (13)) and at δ 3.5– 4.0 ppm (signals (5) and (6)) which showed that the ring opening occurred by acetic acid and water. Percentage of selectivity was calculated by using the peak area of (CH_3-) group from acetic acid (signal (13)) and that of (CH_3-) group from castor oil (signal (17)) at δ 0.8 – 1.0 ppm.

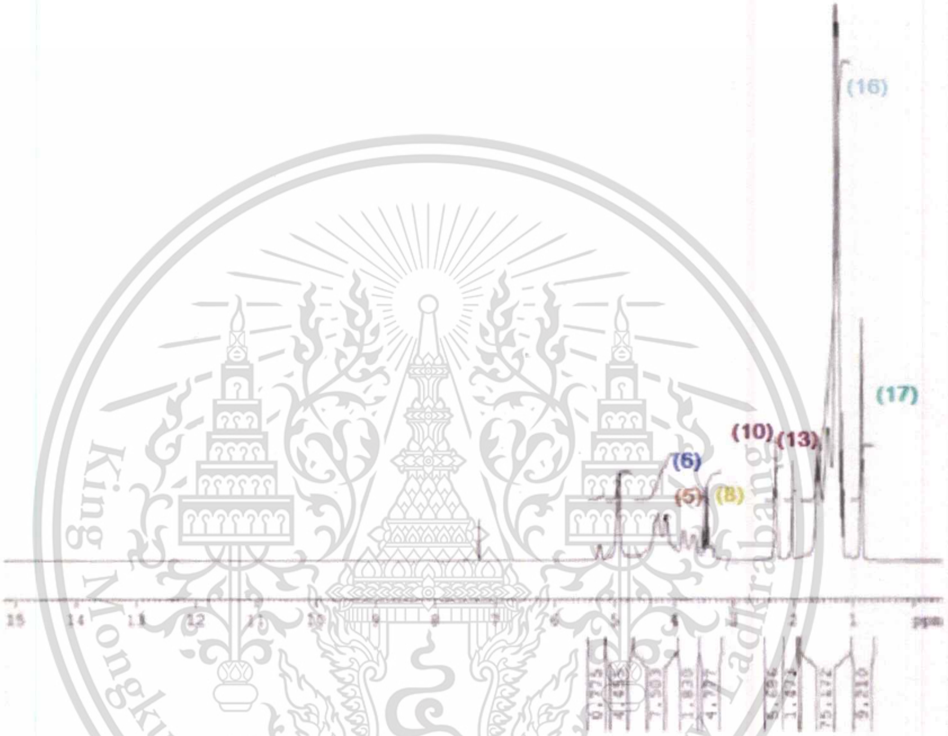


Figure 4.4 ^{1}H-NMR spectrum of product from the reaction using 0.1 mole of castor oil with 2.78 mole of H_2O_2, 0.7 mole of CH_3COOH, and 0.03 mole of H_2SO_4 (Batch 3, Table 3.1)

From Figure 4.4, an example of calculation is shown below the result from

- The % selectivity of epoxide rings opened with acetic acid

$$= \frac{\text{H}-\text{integration of }(\text{CH}_3-)\text{ group from actate}}{\text{H}-\text{integration of }(\text{CH}_3-)\text{ at terminal long chain from castor oil}} \times 100$$

$$= \frac{1.473}{9.210} \times 100$$

$$= 16\ \%$$

where H- integration of (CH_3-) in acetate functional group is at δ 1.9-2.2 ppm and H- integration of (CH_3-) at terminal chain is at δ 0.6-1.0 ppm

- The % selectivity of epoxide rings opened with H_2O

$$= 100 - \%\text{ selectivity of epoxide rings opened with acetic acid}$$

$$= 100 - 16\ \%$$

$$= 84\ \%$$

The results from the first attempt show that 100% conversion of double bond to epoxide ring can be achieved. However, 100% of epoxide ring can be opened which 84% of epoxide ring opened by water and another 16% opened by acetic acid.

Although the result from the first condition gave 100 percent conversion of double bonds and epoxidised ring which was opened by CH_3COOH and H_2O, the second attempt was carried out to reduce the amount of chemicals used and to study whether 100% conversion was still be reached. 0.1 mol of castor oil with 0.75 mol of H_2O_2, 0.20 mol of CH_3COOH, and 0.008 mol of H_2SO_4 were used. The ^{1}H-NMR spectrum of product from this condition showed that double bonds were not completely oxidized since the peaks at δ 5.4-5.8 ppm were observed. Furthermore, the epoxidised rings were not totally opened as the peaks at δ 2.9-3.2 ppm were observed.

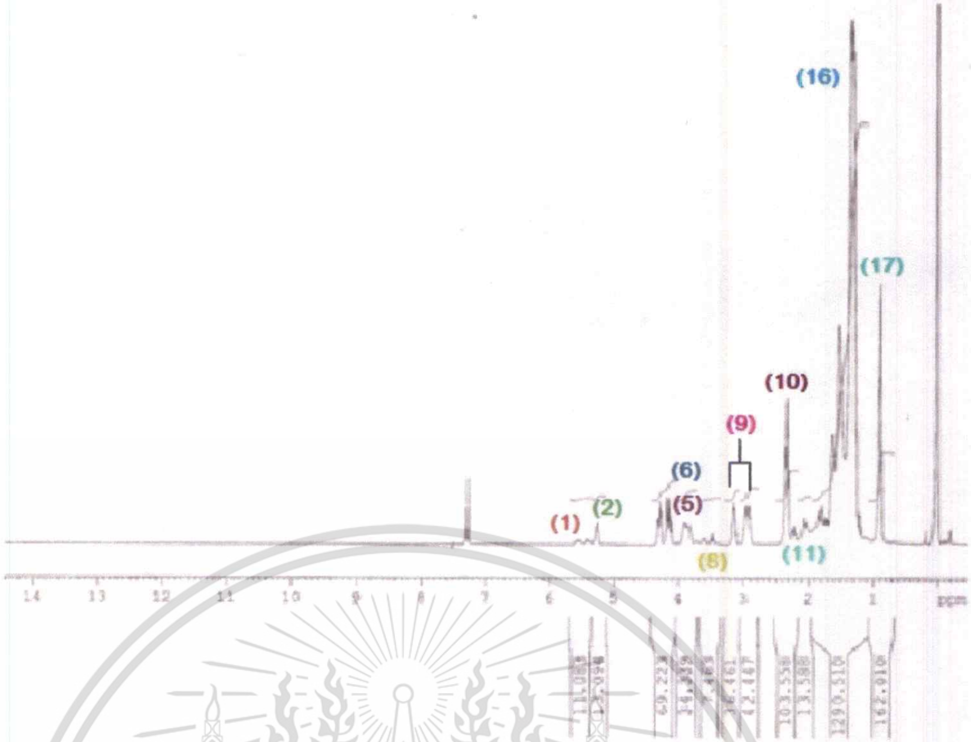


Figure 4.5 ^{1}H-NMR spectrum of production from the reaction using 0.1 mol of castor oil with 0.75 mol of H_2O_2, 0.20 mol of CH_3COOH, and 0.008 mol of H_2SO_4 (Batch 1, Table 3.1)

The final attempt was carried out by using 0.1 mol of castor oil with 1.50 mol of H_2O_2, 0.40 mol of CH_3COOH, and 0.016 mol of H_2SO_4 (Batch 2, Table 3.1). The quantity of chemicals used was double of that used in the second attempt, but still lower than that of the first. The result showed the percent conversion of double bond to be 100% which the disappearance of peak at δ 5.4-5.8 ppm could be observed. In addition, the epoxidised ring was totally opened by 79.10% with water and 20.90% with acetic acid.

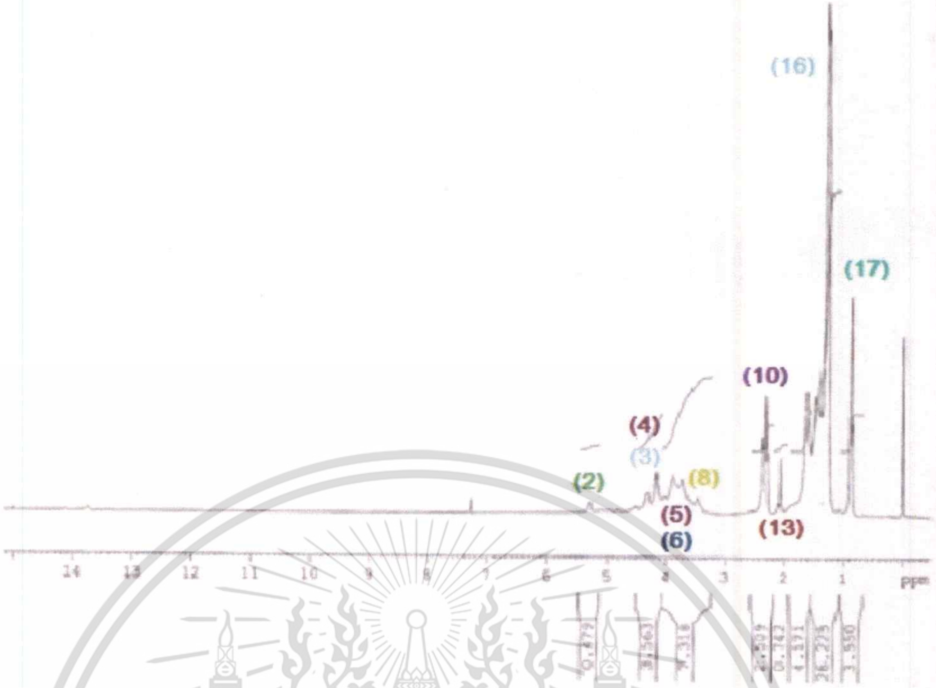


Figure 4.6 ^{1}H-NMR spectrum of production from the reaction using 0.1 mol of castor oil with 1.50 mol of H_2O_2, 0.40 mol of CH_3COOH, and 0.016 mol of H_2SO_4 (Batch 2, Table 3.1)

However, the product from this condition was cloudy and more viscous. It appears that this product has higher percentage of ring opening by acetic acid which could lead to higher degree of chain entanglement compared to the one opened by water. More importantly, the oxygen atoms from ester linkage of acetate lead to high degree of hydrogen bonding. As a consequence, these probably result in the formation of product with higher viscosity and degree of crystallization than that from the first attempt. It makes this product not suitable for use as base oil.

Table 4.2 % Conversion of double bond and % selectivity of ECO derivatives.

Batch	% Conversion of double bond	% Selectiviy of epoxidise ring	
		Opened with H_2O	Opened with CH_3COOH
1	N/A	N/A	N/A
2	100	79.10	20.90
3	100	84.00	16.00

Note: From ^{1}H NMR spectrum % conversion of double bond and % selectivity of products in Batch 1 could not be calculated because of the overlapping of double bond peak with OH peak.

From the above reasons, the condition from the first attempt was used to synthesize base oil for grease preparation. Approximately, one liter of oil was needed for properties testing and grease preparation.

4.2 Properties of synthesized oil

The viscosity and viscosity index of the product were determined by Capillary Tube Viscometer at Petroleum Products and Alternative Fuels Research Department, PPT Research and Technology Institute. In this work, the product had very high viscosity which was difficult to analyze at 40 °C. The viscosity at 40 °C came from the calculation between the viscosity at 60°C and 100°C. Computer software was used to calculate the VI value from the viscosity at 40°C and 100 °C. The results are shown in Table 4.3

Table 4.3 Viscosity of the epoxidised castor oil derivatives

Temperature (°C)	Viscosity (cSt)	VI
100	232.6	97
60	2398	
40	12726	

4.3 Preparation of greases and their properties

The preparation of sodium soap was done by the saponification of palm oil with sodium hydroxide. The appearance of soap could be observed as white solid shown in Figure 4.7. The dropping point and cone penetration of greases were tested using capillary tube viscometer at PPT research and technology institute, and Cone penetrometer at Focuslab Ltd., respectively.

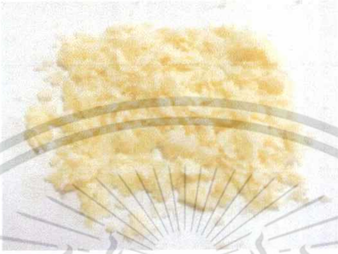


Figure 4.7 Sodium soap

Grease blending was carried out using Moulinex blender as described in section 3.5. The blends with oil/soap ratios of 90:10 and 80:20 were too thin to be used as grease. They flowed very easily as liquid when their bottles were tilted. With oil/soap ratios of 70:30 and 60:40, the products were viscous enough to be tested. For visual observation, the flow ability of products depended largely on the amount of soap. The product of each ratio was, however, completely mixed without oil separation. The appearances of all products are shown in Figure 4.8 and 4.9.

Figure 4.8 The appearance of grease with oil to soap ratio between 90:10 and 80:20

Figure 4.9 The appearance of grease with oil /soap ratio between 70:30 and 60:40

4.3.1 Dropping point

Dropping point is the temperature of grease where the first drop of oil separates from thickener in a perforated cup. Greases commonly used in heavy – duty ball and roller bearing have their typical temperatures limited to a range of 150° to 200° F, approximately 65° **to** 93°C [16]

In this work, the products with oil/soap ratio of 70:30 and 60:40 were used in dropping point testing. The dropping point values are shown in Table 4.4.

Table 4.4 Dropping point tcsting

Base oil: soap ratio	Dropping point (°C)
60:40	109
70:30	106

The results showed that the higher the soap ratio, the higher the dropping point. Moreover, both ratios have dropping point over 100°C. This probably makes these greases have enough stability to be used at normal operating temperature in heavy –duty ball and roller bearings as well as plain bearing applications.

4.3.2 Cone penetration

The consistency of a solid to semi-fluid body is a very complex subject, but the penetration of one body into another one can be measured easily and with simple devices. Grease are named according to consistency classes defined by the US national lubricating grease institute (NLGI) and in accordance with the cone- penetration method

In this work, the products with oil/soap ratio of 60:40 and 70:30 were tested for cone-penetration. The results from cone-penetration are showed in Table 4.5. The word "worked" means the grease sample after used, and the word "unworked" means the new grease.

Table 4.5 Cone penetration testing

Base oil: soap ratio	ASTM penetration	
	worked	unworked
60:40	184.13	132.19
70:30	201.00	168.93

From Table 4.5, the results could be used to classify the products as grease according to NLGI number as shown in Table 4.6. Grease classification according to NLGI (National Lubricating Grease Institute) is explained in Appendix.

Table 4.6 Classification of greases by NLGI numbers

Base oil: soap ratio	NLGI number	
	worked	unworked
60:40	4	5
70:30	4	5

From Table 4.6, these greases could probably be used as hard grease or for rolling contact bearing because the NLGI No.4 is a class suitable for use in rolling contact bearing whereas the NLGI No.5 is a class suitable for use as hard grease.

Chapter 5

Conclusions and Suggestions

5.1 Conclusion

In this research, the reactions to synthesize a lube base from castor oil for use in grease formulation were attempted via acid – catalyzed epoxidation using peracitic acid generated from hydrogen peroxide and acetic acid follow by the ring- opening of deoxidized product. The products under various conditions were or analyzed using ^{1}H NMR spectra. By using 2.78 mol of hydrogen peroxide, 0.70 mol of acetic acid, 0.10 mol of castor oil, and 0.03 mol of H_2SO_4, it was found that double bond was totally oxidized to epoxidised ring which was also totally opened with 84% of water and 16% of acetic acid. The oil product was clear with crystallization. The properties of this product were tested and repeated as follows: viscosity@40°C, 12726 cSt; viscosity @ 60°C, 2396 cSt; viscosity@100°C, 232.6 cSt; viscosity index (VI), 97.

Four grease samples formulation were formulated by blending the oil product with sodium soap using 90/10, 80/20, 70/30, and 60/40 oil/soap ratio. It was found that the greases with 90/10 and 80/20 oil to soap ratios were too thin to be used. They flowed very easily as liquid when their bottles were tilted. Only the ones with 70/30 and 60/40 oil to soap ratios were subjected to the property testings. The dropping points were as follows: dropping point of 60/40 ratio, 109°C; dropping point of 70/30 ratio, 106°C. The cone-penetration were as follows worked penetration of 60/40 ratio, 184.13; unworked penetration of 60/40 ratio, 132.19; worked penetration of 70/30 ratio, 201.00; unworked penetration of 70/30, 168.93. From above reason, these synthetic greases could be classified according to NLGI as greases used in rolling contact bearing, and as hard greases.

5.2 Suggestions

More synthesis could be attempted using less amount of chemical, for instance, by adjustment only the weight of peracetic acid or H_2O_2.

Type of thickener could be changed from sodium soap to other soaps such as lithium soap, calcium soap etc to improve properties.

The other oil containing chains with high amount of double bond of low amount of OH group could be mixed with castor oil to adjust the viscosity of the final product.

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Appendix

Appendix

Calculation

Table 1 Fatty acid composition of drying castor oil

Name	Notation	castor
Oleic	18:1 (9C)	8
Linoleic	18:2 (9C, 12C)	-
∝ —linolenic	18:3 (9C, 12C, 15C)	3
∝ —eleostearic	18:3 (9C, 11t, 15t)	-
Ricinoleic	18:1 (9C) 12-OH	86
Plamitic	16:00	-
Stearic	18:00	2

Table 2 Molecular weight and no. of double bond of castor oil (in form of fatty acid)

Name	Notation	wt % of fatty acid in castor oil	MW of fatty acid in castor oil	wt % x MW of fatty acid in castor oil	wt % x No. of DB.
Oleic	18:1 (9C)	8	282.46	22.8251	0.081
linolenic	18:3 (9C, 12C, 15C)	3	280.1	8.4879	0.091
Ricinoleic	18:1 (9C) 12-OH	86	298.46	259.2683	0.869
Stearic	18:0	2	284.48	5.7471	-
Total	5 DB	99	-	296.3283	1.040

Average molecular weight of castor oil is 296.3283 g/mol (in form of fatty acid)

In form of triglyceride shown in Figure 1, Average molecular weight of castor oil is

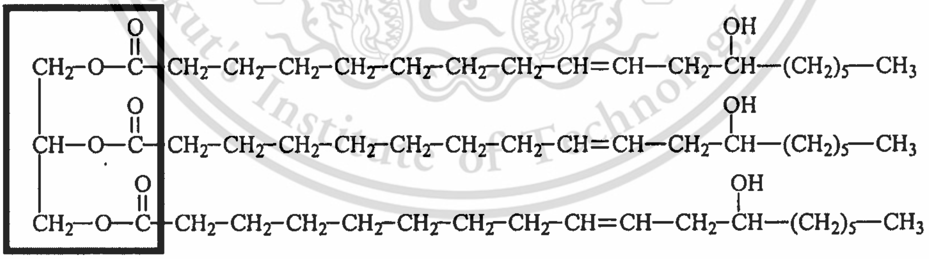

Figure 1 Castor oil structure

(3×296.3283 g/mol (in form of fatty acid)) - 3H + $2CH_2$ + CH

= (3×296.3283)- 3.03 + (2×14.03)+13.02

= 927.0349 g/mol of castor oil in triglyceride form

Average no. of double bond (DB) of castor oil is 1.040 DB/mol (in form of fatty acid)

So, In form of triglyceride, Average no. of double bond (DB) of castor oil is

1.040 DB/mol (in form of fatty acid) ×3 = 3.12 DB/mol

1 mol of castor oil (in form triglyceride) which bond average is 3.12 bonds is 927.03 g/mol

And castor oil is $\frac{927.03\ \mathrm{g/mol}}{3.12\ \mathrm{DB\ mol}}$ = 297.13 g/double bond mole

NLGI consistency number

The NLGI consistency number (sometimes called "NLGI grade") expresses a measure of the relative hardness of a grease used for lubrication, as specified by the standard classification of lubricating grease established by the National Lubricating Grease Institute (NLGI). Reproduced in standards ASTM D 4950 ("standard classification and specification of automotive service greases") and SAE J310 ("automotive lubricating greases"), NLGI's classification is widely used. The NLGI consistency number is also a component of the code specified in standard ISO 6743-9 "lubricants, industrial oils and related products (class L) — classification — part 9: family X (greases)".

The NLGI consistency number alone is not sufficient for specifying the grease required by a particular application. However, it complements other classifications (such as ASTM D4950 and ISO 6743-9). Besides consistency, other properties (such as structural and mechanical stability, apparent viscosity, resistance to oxidation, etc.) can be tested to determine the suitability of a grease to a specific application.

Test methodology

NLGI's classification defines nine grades, each associated to a range of ASTM worked penetration values, and measured using the test defined by standard ASTM D217 "cone penetration of lubricating grease". This involves two test apparatus. The first apparatus consists of a closed container and a piston-like plunger. The face of the plunger is perforated to allow grease to flow from one side of the plunger to another as the plunger is worked up and down. The test grease is inserted into the container and the plunger is stroked 60 times while the test apparatus and grease are maintained at a temperature of 25 °C.

Once worked, the grease is placed in a penetration test apparatus. This apparatus consists of a container, a specially-configured cone and a dial indicator. The container is filled with the grease and the top surface of the grease is smoothed over. The cone is placed so that its tip just touches the grease surface and the dial indicator is set to zero at this position. When the test starts, the weight of the cone will cause it to penetrate into the grease. After a specific time interval the depth of penetration is measured.

Classification

The following table shows the NLGI classification and compares each grade with household products of similar consistency.

Table 3 NLGI consistency numbers

NLGI number	ASTM worked (60 strokes) penetration at 25 °C tenths of a millimeter	Appearance	Consistency food analog
000	445-475	fluid	cooking oil
00	400-430	semi-fluid	applesauce
0	355-385	very soft	brown mustard
1	310-340	soft	tomato paste
2	265-295	"normal" grease	peanut butter
3	220-250	firm	vegetable shortening
4	175-205	very firm	frozen yogurt
5	130-160	hard	smooth pate
6	85-115	very hard	cheddar cheese

Common greases are in the range 1 through 3. Those with a NLGI No. of 000 to 1 are used in low viscosity applications. Examples include enclosed gear drives operating at low speeds and open gearing. Grades 0, 1 and 2 are used in highly loaded gearing. Grades 1 through 4 are often used in rolling contact bearings. Greases with a higher number are firmer, tend to stay in place and are a good choice when leakage is a concern.