ANALYSIS, MODIFICATION AND EVALUATION OF THE COLD FLOW PROPERTIES OF VEGETABLE OILS AS BASE OILS FOR INDUSTRIAL LUBRICANTS

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CERTIFICATE

This is to certify that the thesis entitled "**ANALYSIS, MODIFICATION, AND EVALUATION OF THE COLD FLOW PROPERTIES OF VEGETABLE OILS AS BASE OIL FOR INDUSTRIAL LUBRICANTS**" is a bonafide record of the work done by **Sri.G.Ajithkumar**, under my supervision and guidance. The thesis is submitted to the **Cochin University of Science and Technology, Kochi,** in fulfilment of the requirements for the award of the degree of **Doctor of Philosophy** in the **Faculty of Engineering**. The matter contained in this thesis has not been submitted to any other University or Institute for the award of any degree

CUSAT, Kochi
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Abstract

Poor cold flow properties of vegetable oils are a major problem preventing the usage of many abundantly available vegetable oils as base stocks for industrial lubricants. The major objective of this research is to improve the cold flow properties of vegetable oils by various techniques like additive addition and different chemical modification processes.

Conventional procedure for determining pour point is ASTM D97 method. ASTM D97 method is time consuming and reproducibility of pour point temperatures is poor between laboratories. Differential Scanning Calorimetry (DSC) is a fast, accurate and reproducible method to analyze the thermal activities during cooling/heating of oil. In this work coconut oil has been chosen as representative vegetable oil for the analysis and improvement cold flow properties since it is abundantly available in the tropics and has a very high pour point of 24 °C. DSC is used for the analysis of unmodified and modified vegetable oil. To modify cold flow properties techniques such as additive-addition and chemical modifications were carried out. The modified oils were analyzed by DSC to ascertain the effectiveness of the procedures adopted. Since poor pour point was the major hurdle in the use of vegetable oils as lubricants, the first task was to bring down the pour point to desired level. The modified oils (with acceptable pour points) were then subjected to different tests for the valuation of important lubricant properties such as viscometric, tribological (friction and wear properties), oxidative and corrosion properties.

A commercial polymethacrylate based PPD (obtained from Lubrizol, Chennai, India) was added in different percentages (by weight) from 0.1 to 0.5 and the pour points were determined in each case. Styrenated phenol(SP) was added in different concentration to coconut oil and each solution was subjected to ASTM D97 test and analysis by DSC. The effect of PPD on the pour point of coconut oil was not significant. Addition of SP caused significant reduction of pour point from 24 °C (0% SP) to 12°C (15% SP). But the pour point obtained was still much higher than that is required for any lubricant application (-6°C for two-stroke engine lubricant as per IS14234).

Interestification of coconut oil with other vegetable oils such as castor oil, sunflower oil and keranja oil was attempted to reduce pour point of coconut oil. Refined coconut oil and other oils like castor oil, sunflower oil and keranja oil were mixed in different proportions and interesterification procedure was carried out. Interesterification of coconut oil with other vegetable oils was not found to be effective in lowering the pour point of coconut oil as the reduction attained was only to the extent of 2 to 3 °C. DSC analysis has shown that there is always a peak corresponding to the solidification of the triacylglycerol molecules with predominantly saturated fatty acid content (lauric acid).

Chemical modification by acid catalysed condensation reaction with coconut oil castor oil mixture resulted in significant reduction of pour point (from 24 ℃ to -3 ℃). Instead of using triacylglycerols, when their fatty acid derivatives (lauric acid- the major fatty acid content of coconut oil and oleic acid- the major fatty acid constituents of mono- and poly- unsaturated vegetable oils like olive oil, sunflower oil etc.) were used for the synthesis , the pour point could be brought down to -42 ℃. FTIR and NMR spectroscopy confirmed the ester structure of the product which is fundamental to the biodegradability of vegetable oils. Coconut oil used was commercially available edible grade oil. Oleic acid, castor oil, perchloric acid, 2-ethylhexyl alcohol, and potassium hydroxide were laboratory grade reagents obtained from Aldrich.

The tribological performance of the synthesised product with a suitable AW/EP additive was comparable to the commercial SAE20W30 oil. The viscometric properties (viscosity and viscosity index) were also (with out additives) comparable to commercial lubricants. The TGA experiment confirmed the better oxidative performance of the product compared to vegetable oils. The sample passed corrosion test as per ASTM D130 method.

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Nomenclature

List of Symbols

C6:0	Caproic acid
C8:0	Caprylic acid
C10:0	Capric acid
C12:0	Lauric acid
C14:0	Myristic acid
C16:0	Palmitic acid
C18:0	Stearic acid
C18:1	Oleic acid
C18:2	Linoleic acid
μ	Coefficient of friction

Acronyms

2T oil	Two-stroke engine oil
AW/EP	Anti-wear/extreme pressure
CMM	Co-ordinate measuring machine
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Derivative thermogravimetric
FTIR	Fourier transform infrared
FTNMR	Fourier transform nuclear magnetic resonance
IE	Interesterification
GC-MS	Gas chromatography-mass spectroscopy
LD_{50}	Lethal dose for 50% of the population (measure of toxicity)

MP	Melting point
PP	Pour point
PPD	Pour point depressant
SP	Styrenated phenol
TGA	Thermogravimetric analysis
VII	Viscosity index improvers
WSD	Wear scar diameter
ZDDP	Zinc dialkyldithiophosphate

Chapter 1

Introduction

1.1 Relevance of the Study

Worldwide consumption of lubricants in 2005 was around 40 million metric tonnes and approximately 30% of the lubricants consumed ended up in ecosystem (Bartz, 2006). Present production of biodegradable lubricant is only 1% of the total production (Bartz, 2006). A lubricant consists of a base oil (>90%) and an additive package (<10%). The base oil used for the formulation of most lubricants is environmentally hostile mineral oil. Formulation of environment friendly lubricants depends primarily on the biodegradability of the base oils. Thus search for environment friendly substitutes to mineral oils as base oils in lubricants has become a frontier area of research in the lubricant industry in the new paradigm of sustainable technology development caused by the alarms of environmental degradations. The demand for biodegradable lubricants is due to a growing concern for the impact that technology is making to the environment. This concern is occurring both as the result of a combination of local and national regulations, and as well as a result of consumer influence.

Vegetable oils are perceived to be alternatives to mineral oils for lubricant base oils because of certain inherent technical properties and their ability for biodegradability. Compared to mineral oils, vegetable oils in general possess high flash point, high viscosity index, high lubricity and low evaporative loss(Erhan and Asadauskas, S., 2000; Adhvaryu and Erhan, 2002; Mercurio, *et al.*, 2004). Poor oxidative and hydrolytic stability, high temperature sensitivity of tribological behaviour and poor cold flow properties are reckoned to be the limitations of vegetable oils for their use as base oils for industrial lubricants(Erhan and Asadaukas, 2000; Adhvaryu *et al.*, 2005). Elaborate literature survey revealed that many technical solutions such as chemical modification and additivation have been suggested to overcome the poor oxidative and hydrolytic stability and high temperature sensitivity of tribological behaviour of vegetable oils when used as base oils for lubricants. The wide spread use of vegetable oils as lubricants was limited in colder countries even in pre-mineral oil era because of their high congelation temperature. Detailed literature survey also indicated a certain dearth of knowledge in the analysis and improvement of cold flow properties of vegetable oils. Reaction to heat and pressure by vegetable oils is found to be intriguing because of the heterogeneous and complex ester structure. The present study is intended to bridge this gap in the investigations on the behaviour of vegetable oils when used as base oils for industrial lubricants.

In the face of expanding market for environment friendly lubricants forced by legislations and public opinion, the present work is significant as it aspires to expand the knowledge base on the behaviour of vegetable oils when used as base oils for industrial lubricants.

1.2 Vegetable Oils and Lubricants

Vegetable oils have been used as lubricating oils from ancient days (Dowson, 1998). They are easily obtained from natural sources. Therefore, they had been the main ingredient of lubricating oils until the 19th century. The requirement of lubricants became very high thereafter because of rapid industrialisation, putting pressure on the price and availability of lubricants from vegetable and animal sources. Mineral oils were started being used as lubricating oils after the successful prospecting and extraction of mineral oils during the second half of 19th century which made available large quantities of cheap replacement for lubricants of vegetable and animal origin. Mineral oils provide various fluids which have desirable properties as lubricating oils at a reasonable cost. For that reason, most of the lubricating oils are supplied from petroleum-based materials. Recently, demand for environmentally friendly lubricants are increasing because of the high concern for environmental protection. Vegetable oils are natural products and, in addition, they are recognized as a fast biodegradable fluid. Therefore, they are promising candidates for the base oils of the environmentally friendly lubricating oils (Asadauskas *et al.*, 1996). Lubricants based on mineral oils have been used in all kinds of applications since the beginning of industrialization including industrial gears, automotive engines, metalworking applications transmission and hydraulic systems. But soon it was found that mineral oil with the same viscosity as that of the vegetable or animal based oils was not as effective as a lubricant as the latter. This was attributed to a property of the vegetable or animal oils and fats called “oiliness” or “lubricity” (Ratoi *et al.*, 2000). Lubricity or oiliness of vegetable oils is attributed to their ability to adsorb to the metallic surfaces and to form a tenacious monolayer, with the polar head adhering to the metallic surfaces and the hydrocarbon chains orienting in near normal directions to the surface (Weijiu *et al.*, 2003) as depicted in Figure. 1.1.

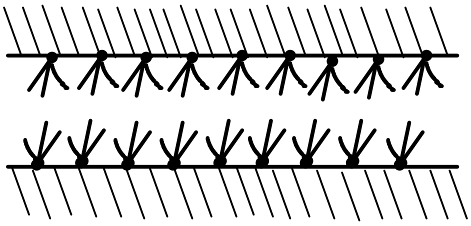


Figure 1.1: Monolayer of vegetable oil molecules adsorbed on metallic surfaces

To impart "oiliness" to mineral oil based lubricants, a small percentage of vegetable or animal oil started being added to it as "oiliness" additive. Later many organic, inorganic and polymer additives for mineral oil based lubricants were developed to meet the more and more severe operating requirements made on the lubricants used in various applications such as high speed and high performance internal combustion engines. The physical and to some extent chemical properties of mineral oil based lubricants have been studied for almost as long. Lubricant manufacturers have, over the years, gathered know-how and the necessary technologies to blend lubricants to give the required performance. Different kinds of additives are used to improve the performance and longevity of lubricants. Depending on the specific demands and performance level requirements, several different classes of additives may be used. These include detergents, dispersants, extreme pressure (EP), anti-wear (AW), viscosity index improvers (VII), and corrosion inhibitors (Rizvi, 1999). The state of the art industrial lubricant consists of base oil and an additive package.

Many countries including Austria, Canada, Hungary, Japan, Poland, Scandinavia, Switzerland, the USA, and EU are either in the process of formulating or have already passed legislation to regulate the use of mineral oil based lubricants in environmentally sensitive areas (Bartz, 1998; Bartz, 2006). The U.S. market for all lubricants is 8,250,000 tons/year and only 25,000 tons/year were based on vegetable oils (Whitby, 2004). In the USA, executive order 12873 (EQ 12873) encourages the use of environmentally compatible oils where it is possible to meet the requirements. Similarly, the Great Lakes Water Quality Initiative (GLWQI) in the USA is intended to maintain, protect, and restore the unique Great Lakes resource (e.g. water quality). Within GLWQI, there are proposals to encourage use of fast biodegradable lubricating oils and limiting the use of potentially toxic (to aquatic life) additives to very low levels. In Austria use of mineral-based lubricants, in particular applications like chain saw oils are banned. Recently the European Community (EU) has released the Dangerous Substances Directive. It establishes criteria for a product's potential hazards to aquatic environment. This hazard potential is determined through assessment of aquatic toxicity, biodegradability, and bioaccumulation potential. The other countries mentioned above have at least established regulations to evaluate the lubricant caused impairment to the environment.

The performance limitations of vegetable-based lubricants stem from inherent properties of the vegetable oil base stocks rather than composition of additive package. Base stocks usually comprise more than 90% of the lubricants and nearly entirely pre-define properties such as high biodegradability, low volatility, ideal cleanliness, high solvency for lubricant additives, miscibility with other types of system fluids, negligible effects on seals and elastomers, and other less significant properties (e.g. density or heat conductivity) (Erhan and Asadaukas, 2000). Base stocks are also a major factor in determining oxidative stability, deposit forming tendencies, low temperature solidification, hydrolytic stability, and viscometric properties. On the other hand, parameters like lubricity, wear protection, load carrying capacity, corrosion (rust) prevention, acidity, ash content, colour, foaming, de-emulsification (so called demulsibility), water rejection, and a number of others are mostly dependent on the additives or impurities/contaminants (Erhan and Asadaukas, 2000). Therefore, when a given fluid is considered for its suitability as a lubricant, first of all, the base stock-dependent parameters are evaluated. In addition to biodegradability, the following characteristics must be given attention: cleanliness (particle count), compatibility with mineral oil lubricants, homogeneity during long term storage, water content and acidity, viscosity, viscosity index, pour point, cloud point, cold storage, volatility, oxidative stability, elastomer compatibility and possibly other properties, depending on intended application. Water rejection, demulsibility, corrosion protection, ash content and foaming could also be tested if contamination of the additive-free oil is suspected.

From a technical point of view, it is accepted that more than 90% of all present-day lubricants could be formulated to be rapidly biodegradable (Wagner *et al.*, 2001). On the other hand, a great deal of development work still needs to be done and present costs are high (Mang, 1997; Hill, 2000). Vegetable products as well as modified vegetable oil esters can be used as a base stock for preparation of environment friendly, rapidly biodegradable lubricants. The production of environment friendly, rapidly biodegradable fluids for lubricants based on petrochemicals such as polyalphaolefins, polyglycols, polyalkylene glycols and synthetic esters are also discussed in literature (Mang, 1997; van Voorst and Alam, 2000). However, vegetable oils are preferred over these synthetic fluids because they are from renewable resources and cheaper (Adhvaryu and Erhan, 2005).

Some of the rapidly biodegradable lubricants are based on pure, unmodified vegetable oils. In Europe, predominantly rapeseed oil and sunflower oil are used (Wagner *et al.*, 2001). Chemically, these are esters of glycerine and long-chain fatty acids (triglycerides). The alcohol component (glycerine) is the same in almost all vegetable oils. The fatty acid components are plant-specific and therefore variable. The fatty acids found in natural vegetable oils differ in chain length and number of double bonds. Besides, functional groups like hydroxyl groups as in castor oil may be present. Natural triglycerides are very rapidly biodegradable and are highly effective lubricants. However, their thermal, oxidative and hydrolytic stabilities are limited. Therefore, pure vegetable oils are only used in applications with low thermal stress. These include total loss applications like mold release and chain saw oils.

Though vegetable oils exhibit excellent lubricity at low temperatures, they are known to cause increased wear at high temperatures and under sliding conditions. Choi *et al.* (1997) showed that olive oil and soybean oil exhibit high amount of wear when tested at 150ºC above a sliding speed of 0.4 m/s. Fatty acid constituents of vegetable oils show increased wear above certain transition temperatures (Bowden and Tabor, 2001). The transition temperature depends on individual fatty acids, the nature of the lubricated metals, and on the load and speed of sliding.

The reason for the thermal and oxidative instability of vegetable oils is the structural "double bond" elements in the fatty acid part and the "β-CH group" of the alcoholic (glycerine) components (Wagner *et al.*, 2001). In particular, multiple double bonds are a hindrance for technical application. The bis-allylic protons present in alkenyl chains with multiple bonds are highly susceptible to radical attack and subsequently undergo oxidative degradation and form polar oxy compounds (Adhvaryu *et al.*, 2005). This phenomena result in insoluble deposits and increase in oil acidity and viscosity. Vegetable oils also show poor corrosion protection especially when moisture is present. The β-hydrogen atom is easily eliminated from the molecular structure. This leads to the cleavage of the esters into acid and olefin. A further weakness of natural esters is their tendency to hydrolyze in the presence of water (Goyan *et al.*, 1998).Therefore, contamination with water in the form of emulsion must be prevented at every stage.

Low temperature study has also shown that most vegetable oils (unsaturated) undergo cloudiness, precipitation, poor flow, and solidification at ~ -10ºC upon long-term exposure to cold temperature, in sharp contrast to mineral oil-based fluids (Rhee *et al.*, 1995; Kassfeldt and Goran, 1997). Saturated vegetable oils, like coconut oil show much poorer cold flow characteristics with pour point at ~25 ºC. Over a hundred cases have been reported on melting temperatures of mainly monoacid triacylglycerols (Hagemann,1988). However, crystalline forms of unsaturated triacylglycerols have been established only for triacylglycerols with symmetrical distribution of monounsaturated fatty acids. Thus investigations of crystallization of unsaturated mixed acid triacylglycerols are mostly empirical (D'Souza *et al.*, 1991), and solidification of such triacylglycerols is too complex to be studied using traditional techniques, such as X-ray diffraction. Nonetheless, it has been firmly established (Larsson,1994; Hagemann,1988) that presence of cis unsaturation, lower molecular weights, and diverse chemical structures of triacylglycerols favour lower temperatures of solidification.

Poor low-temperature properties include cloudiness, precipitation, poor flowability, and solidification at relatively high temperatures (Asadauskas *et al.*, 1996). Efforts have been made to improve the low temperature properties by blending the vegetable oils with diluents such as poly α olefin, diisodecyl adipate, and oleates (Asadauskas *et al.*, 1999). The other possible way to control these obstacles is structural modification of the oils by chemical reaction (Randles and Wright, 1992). It has been reported that triacylglycerols with more diverse chemical structures have lower solidification temperatures. (Ohkawa *et al.*, 1995; Rhodes *et al.*, 1995). Vegetable oils are mostly split into their oleochemical components such as fatty acids or fatty acid methylesters and glycerine before they are modified. Fatty alcohols can be formed out of fatty acid methylesters. However, the vegetable oil can be directly modified, for example,by direct transesterification or selective hydrogenation. The most important modifications concern the carboxyl group of the fatty acids. They accounts for about 90% of the oleochemical reactions, whereas reactions of the fatty acid chain only account for less than 10% (Kassfeldt and Goran, 1997; Rhee *et al.*, 1995).

1.3 Definition of the Problem

Poor cold flow properties of vegetable oils are a major problem preventing the usage of many abundantly available vegetable as base stocks for industrial lubricants. Conventional methods of determining cold flow properties especially the pour point (by ASTM D97 method) of vegetable oils are time consuming and their repeatability is poor. While cooling vegetable oil crystallizes in to different polymorphs depending up on the rate of cooling. If the cooling rate is high vegetable oils will crystallize in to the low melting α polymorph giving a low pour point value. But if the vegetable oil is kept at the 'pour point' temperature for a prolonged period of time it will re-crystallize into higher melting polymorphs and congeal. DSC is a thermo-analytical tool widely used in chemical and pharmaceutical industries. DSC is capable of picking up all kinds of thermal activities like crystallization, melting, glass transition etc while heating and cooling with high accuracy and repeatability. In the present work coconut oil is chosen as representative vegetable oil for the analysis and improvement cold flow properties since it is abundantly available in the tropics and has a very high pour point of 24 ºC. DSC is used for the analysis of unmodified and modified vegetable oils.

1.4 Objectives of the Study

The present work is envisaged;

1. To improve the cold flow properties of the selected vegetable oil by various techniques like additive addition and different chemical modification processes
2. To evaluate the effectiveness of additive addition and different chemical modification processes by DSC.
3. To chemically characterise the modified vegetable oil by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.
4. To evaluate the important lubricant properties such as viscometric, tribological and oxidative properties of the modified vegetable oil using standard tests and procedures.

1.5 Methodology

The details of the methodology adopted in this work are as follows;

1. Detailed analysis and evaluation of the effectiveness of PPDs in the improvement of cold flow properties of vegetable oils. New generation thermal analysis methods like DSC are used for the analysis of cold flow properties and their improvements by PPDs.
2. Detailed analysis and evaluation of the effect of random esterification in mixtures of vegetable oils and its effect on cold flow properties is investigated. DSC is used to analyse the cold flow properties of interesterified vegetable oils.
3. Synthesis of estolides and their esters from vegetable oils and their fatty acid constituents is undertaken. DSC is used as the evaluation tool of the cold flow properties of synthesised estolides.

4. Evaluation of the important lubricant properties of products synthesized such as physicochemical properties, viscometric, tribological and oxidative properties and chemical characterization of the products using FTIR and NMR spectroscopy.

1.6 Structure of the Thesis

The present work is structured into seven Chapters

In Chapter 1 of the thesis the relevance, background, and objectives of the work are presented. The properties of vegetable oils in respect of their use as base oils and the advantages and shortcomings of vegetable oils are also discussed in Chapter 1.

A comprehensive review of the literature related to the environmental aspects of the use of vegetable oil as base oil for industrial lubricants and low temperature properties of vegetable oils and their evaluation techniques are presented in Chapter 2.

In Chapter 3 detailed analyses and evaluation of effectiveness of Pour Point Depressants in the improvement of cold flow properties of vegetable oils are given .The use of new generation thermal analysis methods like DSC for the analysis of cold flow properties and their improvements by PPDs are also elaborated.

Interestification is a method to randomise the distribution of fatty acids on individual triacyl fatty acid molecules. Chapter 4 narrates the attempts to lower pour points of vegetable oils by interesterification.

Chapter 5 discusses the synthesis of estolides (fatty acid olygomers) from mixtures of vegetable oils and their constituents and the use of Differential Scanning Calorimetry for the evaluation of the cold flow properties of estolides (fatty acid olygomers) so synthesised .

An account of the evaluation of lubrication properties of esterified estolides such as physicochemical properties, viscometric, tribological and corrosion properties is detailed in Chapter 6.

Chapter 7 presents the summary and conclusion of the present study. This chapter also highlights the scope for future work and significance of the findings presented in the thesis.

Chapter 2

Literature Survey

2.1 Introduction

The objective of the work reported in this thesis is to analyse and improve the low temperature properties of vegetable oils for use as base oils for lubricants based on its chemical composition and molecular structure. Composition and molecular structure determines the properties, stability and degradation of vegetable oils. In addition, chemical modifications are an important route to improve the properties of vegetable oils including low temperature properties of vegetable oils. Vegetable oils are perceived as base oil replacements for mineral oils in lubricants essentially because of their superior environmental properties. Hence, a detailed review of the composition, structure and chemical reaction mechanisms of vegetable oils, their environmental and physio-chemical properties are presented in the following sections.

2.2 Chemistry Of Vegetable oils

2.2.1 Composition

Vegetable oils are part of a larger family of chemical compounds known as fats or lipids. They are made up predominantly of triesters of glycerol with fatty acids and commonly are called triglycerides. Lipids are widely distributed in nature; they are derived from vegetable, animal and marine sources and often are by-products in the production of vegetable proteins or fibers and animal and marine proteins. Lipids of all types have been used throughout the ages as foods, fuels, lubricants, and starting materials for other chemicals. This wide utility results from the unique chemical structures and physical properties of lipids. The chemical structures of lipids are very complex owing to the combination and permutations of fatty acids that can be esterified at the three (enzymatically non-equivalent) hydroxyl groups of glycerol. A generalized triglyceride has the structure shown in Figure 2.1, without regard to optical activity (Wallace, 1978).

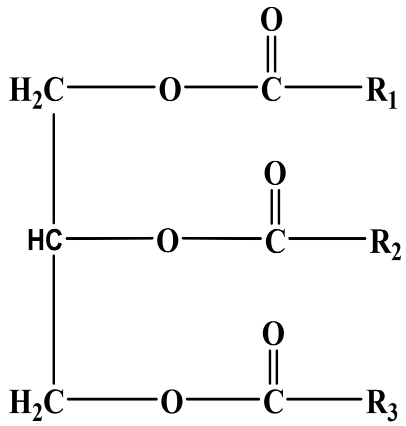


Figure 2.1: The general structure of a triglyceride

When $R_1 = R_2 = R_3$, the trivial name of the triglyceride is derived from the parent acid by means of a termination -in, e.g. for stearic acid where $R_1 = R_2 = R_3 = C_{17}H_{35}$ the triglyceride is called tristearin. If, on the other hand, R_1 and R_3 are different, the centre carbon is asymmetric and the chiral glyceride molecule can exist in two enantiomeric forms (Smith, 1972). Thus, because the fatty acid portions of the triglycerides make up the larger proportion (ca 90% fatty acids to 10% glycerol) of the fat molecules, most of the chemical and physical properties result from the effects of the various fatty acids esterified with glycerol (Wallace, 1978). Fatty acids have a polar head and a hydrocarbon chain. Hydrocarbon chains of fatty acids may contain one or more double bonds. Presence of double bonds and their relative position with respect to the carbon atom of the polar head group (carbonyl carbon) provide fatty acids their characteristic properties. In triglycerides, fatty acids are bonded to the glycerol molecule by eliminating three water molecules.

Naturally occurring fats contain small amounts of soluble, minor constituents: pigments (carotenoids, chlorophyll, etc), sterols (phytosterols in plants, cholesterol in animals), phospholipids, lipoproteins, glycolipids, hydrocarbons, vitamin E (tocopherol), vitamin A (from carotenes), vitamin D (calciferol), waxes (esters of long-chain alcohols and fatty acids), ethers, and degradation products of fatty acids, proteins, and carbohydrates. Most of these minor compounds are removed in processing and some are valuable by-products.

Most of the fatty acids in vegetable oils are esterified with glycerol to form glycerides. However, in some oils, particularly where abuse of the raw materials has occurred leading to enzymatic activity, considerable (>5%) free fatty acid is found. Hydrolysis occurs in the presence of moisture. This reaction is catalyzed by some enzymes, acids, bases, and heat. Table 2.1 lists fatty acid prevalent in fats with their principal natural source and systematic designations (Smith, 1972; Wallace, 1978; Akoh and Min, 2002). Table 2.2 shows how these fatty acids are distributed in the commercially significant fats (Smith, 1972; Wallace, 1978; Akoh and Min, 2002; Gunstone, 1999).

Table: 2.1 Chemical compositions of oils (Fatty acid profiles)

Fatty acid	**Common Name (designation)**[a]	**Source**
Hexanoic	caproic (6:0)	butter, coconut
Octanoic	caprylic (8:0)	Coconut
Decanoic	capric (10:0)	Coconut
Dodecanoic	lauric (12:0)	coconut, palm kernel
Tetradecanoic	myristic (14:0)	coconut, palm kernel, butter
Hexadecanoic	palmitic (16:0)	palm, cotton, butter, animal and marine fat
cis-9-hexadecenoic	palmitoleic (16 :1)	butter, animal fat
Octadecanoic	stearic (18:0)	butter, animal fat
cis-9-octadecenoic	oleic (18 :1, 9c)	olive, tall, peanut, butter, animal and marine fat
cis,*cis*-9,12-octadecadienoic	linoleic (18 :2, 9c,12c)	safflower, sesame, sunflower, corn, soy, cotton
cis,*cis*,*cis*-9,12,15-octadecatrienoic	linolenic (18 :3, 9c,12c,15c)	Linseed
12-hydroxy-*cis*-9-octadecenoic	ricinoleic (18:1, 9c, 12-OH)	Castor
eicosanoic	arachidic (20:0)	groundnut oil, fish oil
cis-11-eicosenoic	(20:1, 11c)	Rapeseed
docosanoic	behenic (22:0)	Rapeseed
cis-13-docosenoic	erucic (22:1, 13c)	Rapeseed

Table 2.2: Distribution of fatty acids in commercially significant fats (Smith, 1972; Wallace, 1978; Akoh and Min, 2002; Gunstone, 1999)

Fat	**Fatty acid composition (wt %)**							**Other acids (wt %)**
	12:0[a]	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	
castor			0,8-1,1	0,7-1,0	2,0-3,3	4,1-4,7	0,5-0,7	ricinolenic (89), 20:1(0,5)
coconut	44-51	13-18,5	7,5-10,5	1-3	5-8,2	1,0-2,6		8:0 (7,8-9,5), 10:0 (4,5-9,7)
corn			7	3	43	39		
cottonseed		1,5	22	5	19	50		
linseed			6	4	13-37	5-23	26-58	
mustard			3	1	23	9	10	20:1(8), 22:1 (43), other (3)
olive		1,3	7-16	1,4-3,3	64-84	4-15		
palm		0,6-2,4	32-45	4-6,3	38-53	6-12		
palm kernel	47-52	14-17,5	6,5-8,8	1-2,5	10-18	0,7-1,3		8:0 (2,7-4,3), 10:0(3-7)
groundnut		0,5	6-11,4	3-6	42,3-61	13-33,5		20:0 (1,5), 20:1+2 (1-1,5), 22:0(3-3.5)
rapeseed regular		1,5	1-4,7	1-3,5	13-38	9,5-22	1-10	22:1 erucic (40-64)
safflower regular			6,4-7	2,4-2,8	9,7-13,1	77-80		20:1 (0,5)
safflower high oleic			4-8	4-8	74-79	11-19		
sesame			7,2-7,7	7,2-7,7	35-46	35-48		
soybean			2,3-10,6	2,4-6	23,5-31	49-51,5	2-10,5	
sunflower			3,5-6,5	1,3-3	14-43	44-68		
Keranja (Pongamia)			11-12	7-8	51-52	16-17		20:1(1-2),22:0(4-5),24:0(1-2)

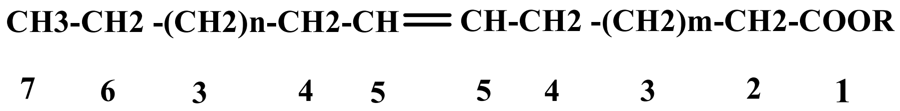
[a] number or carbon atoms: number of unsaturation

2.2.2 Chemistry of Vegetable Oils

All crude vegetable oils contain some natural elements such as unsaponifiable matter, gummy, and waxy matter that may interfere with the stability, hydrocarbon solubility, chemical transformation reactions, and freezing point, and so forth. Therefore, a purification step is required to obtain refined vegetable oils that are completely miscible with hexane. Refined vegetable oils are largely glycerides of the fatty acids. However, to modify the fatty acid chain of the oil, it is necessary to know the exact composition of these oils and their thermal and oxidative properties. It gives indications of likely characteristics of the products formed after chemical modification and the most likely transformations, which are required to improve the physicochemical and performance characteristics of these vegetable oil derivatives. The triacylglycerol structure form the backbone of most vegetable oils and these are associated with different fatty acid chains. It is therefore a complex association of different fatty acid molecules attached to a single triglycerol structure that constitutes vegetable oil matrix (Figure 2.1). The presence of unsaturation in triacylglycerol molecule due to C=C from oleic, linoleic, and linolenic acid moeties functions as the active sites for various oxidation reactions. Saturated fatty acids have relatively high oxidation stability. Soybean oil has more poly-unsaturation (more C18:2 and C18:3) as compared to canola and rapeseed oil. Therefore, SBO needs chemical modification to reduce unsaturation in triacylglycerol molecule and suitable additives to bring its performance equal to or better than other commercial vegetable oils. More than 90% of chemical modifications have been those occurring at the fatty acid carboxyl groups, while less than 10% have involved reactions at fatty acid hydrocarbon chain (Richtler and Knaut, 1984). Chemical modifications of vegetable oils for them to be used as lubricant base oils without sacrificing favourable viscosity–temperature characteristics and lubricity can be classified into two groups: reactions on the hydrocarbon chain and reaction on the carboxyl group.

a) Reactions on the hydrocarbon chain

A model of lipid shown Figure 2.2 can explain the reactive centres in the molecule of a lipid. The ending methyl group (group 7), also known as ω-group, has the highest dissociation energy for the C-H bond; however, it exhibits the lowest steric hindrance for chemical reactions. Enzymatic reactions are until now the only known procedure to selectively activate this group



$$\underset{7}{CH_3}-\underset{6}{CH_2}-\underset{3}{(CH_2)_n}-\underset{4}{CH_2}-\underset{5}{CH}=\underset{5}{CH}-\underset{4}{CH_2}-\underset{3}{(CH_2)_m}-\underset{2}{CH_2}-\underset{1}{COOR}$$

Figure 2.2: Representation of a fatty acid

The α-methyl group (group 2) is activated by the neighbour carboxyl or ester group. Accordingly, it is feasible to perform several selective modifications on this group such as α-sulphonation (Stirton, 1962), α-halogenation (Watson, 1930) (Hell-Volhard-Zelinsky reaction), Claisen condensation (Claisen, 1887), alkylation (Pfeffer, and Silbert, 1972), acylation (Rathke, and Deitch, 1971), and addition of carbonyl compounds.

On the saturated hydrocarbon chain (groups 3) all typical substitution reactions for paraffins are possible in theory. However, the groups closer to the carboxyl group are hindered by its inductive effect. For the other groups, the substitution is statistically distributed.

The allyl position (group 4) is capable of substitution reactions like allyl-halogenation (Ziegler, *et al.*, 1942; Naudet, and Ucciani, 1971), allyl-hydroxylation (Waitkins, and Clark, 1945), electrochemical acetylation (Adams, *et al.*, 1979; Dejarlains, *et al.*, 1988) and allyl-hydroperoxidation (Adams, *et al.*, 1979). The latter reaction will be described separately later because it explains the way how fats oxidatively degrade, which is one of the problems vegetable oils present for uses such as lubricants.

The double bonds in the hydrocarbon chain of oleochemicals exhibit a higher chemical potential than the paraffinic methyl and methylene groups. On the industrial level, chemical reactions on the un-saturation are in second place after the reactions involving carboxylic/ester groups. In industry, the most extensively applied reactions on the un-saturation are hydrogenation and epoxidation. Other reactions with a lower industrial use are isomerization, hydroxylation, oxidative cleavage, metathesis, Diels-Alder reactions, carboxylations (hydroformylation and hydrocarboxylation), and radical and cationic additions.

The *cis*-*trans* isomerization of double bonds converts the less thermodynamically stable *cis*-isomers into the more stable *trans*-isomers (Rheineck, 1958). For example, *cis*-9-octadecenoic acid, which has a low melting point of 16°C, can be transformed to *trans*-9-octadecenoic acid with a higher melting point of 51 °C. Poly-unsaturated acids/esters with isolated double bonds can be converted to the more thermodynamically stable conjugated counterparts through a positional re-localization isomerization (Destaillats and

Angers, 2002). These conjugated fatty acids/derivatives are reactive for Diels-Alders reactions. Alkaline hydroxides in alcoholic solution, potassium alkoxide (or other alcoxides), nickel/activated coal and iron pentacarbonyl ($Fe(CO)_5$) are examples of suitable catalysts for the isomerization of isolated double bonds to produce the conjugated arrangement. The double bond of mono-unsaturated fats can be re-localized using acid catalysts like montmorillonite, solid phosphoric acid (H_3PO_4 on silica) or perchloric acid (Shepard and Showell, 1969).

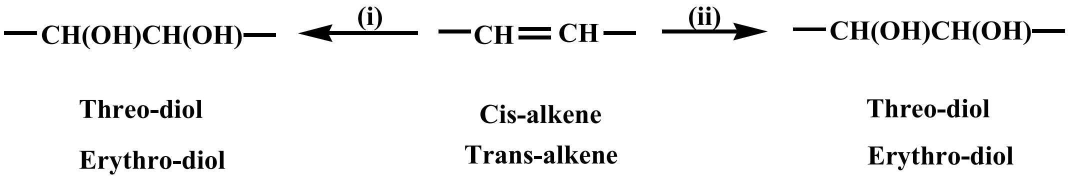
Hydrogenation

Nickel catalyzed hydrogenation of unsaturated fats is carried out in large scale to improve the stability and colour of the fat and to increase the melting point. However, the selective hydrogenation of poly-unsaturated fats is a problem still not fully solved. In industrial processes, heterogeneous catalysts such as carrier catalysts (palladium on active carbon), skeletal catalysts (Raney-Nickel) or metal oxide catalysts (copper-chrome oxide) are mostly used (Wagner *et al*., 2001).

Selective hydrogenation, in which the fatty acid residue is not fully saturated, is of greatest interest in the area of lubricant chemistry. Natural fats and oils often contain multiple unsaturated fatty acids such as linoleic and linolenic acids, which seriously impair the ageing stability of the oil even if they are present in very small quantities. Selective hydrogenation can transform the multiple unsaturated fatty acids into single unsaturated fatty acids without increasing the saturated part of the substance. This is necessary to avoid deterioration in low-temperature behaviour such as on the pour point. Not necessarily needed but sometimes resulting from selective hydrogenation is the formation of configurational- and *cis*/*trans*-isomers of the remaining double bonds. By selective hydrogenation, the easily oxidisable compounds are transformed into more stable components. This significantly improves the ageing behaviour of the oils.

Oxidation to vicinal-dihydroxylated products (glycols)

An alkene can be converted to a diol by reagents, which effect *cis* or *trans* addition and diols have threo or erythreo configuration as shown in Figure 2.3 (Gunstone, 1999). Vicinal-dihydroxylated fats, useful as polyols for polyurethane synthesis, can be produced via the water ring opening of the epoxidized fat. Nonetheless, because the reaction conditions for this procedure are rather drastic (Dahlke, 1995), the direct synthesis of the diol is an interesting reaction. Hydroxylation of oleic acid with H_2O_2 catalyzed by Mo, W or Re compounds also gives the respective diol with the epoxide as intermediate (Adhvaryu *et al.*, 2005; Luong *et al.*, 1967)



(i) Trans-hydroxylation by I_2, AgOCOPh (anhydrous) or epoxydation followed by acid catalyzed hydrolysis
(ii) Cis-hydroxylation by dilute alkaline $KMnO_4$; I_2, AgOAc, AcOH (moist); OsO4.

Figure 2.3: Conversion of alkenes to vicinal diols

Oxidative cleavage

Cleavage of oleic acid to nonanoic acid (pelargonic acid) and di-nonanoic acid (azelaic acid) with ozone (Figure 2.4) is the most important industrial use of ozonolyis (Baumann *et al.*, 1988). It is of high interest to find a catalytic alternative that uses a safer oxidation agent. Direct oxidative cleavage of inner double bonds with peracetic acid and ruthenium catalysts or with H_2O_2 and Re, W and Mo catalysts gives 50-60% yield.

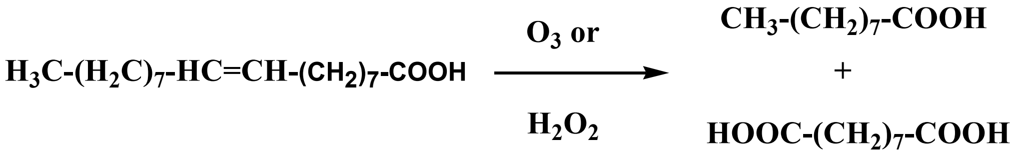


Figure 2.4: Oxidative cleavage of oleic acid

Metathesis

Olefin metathesis is the catalytic exchange of groups attached to a double bond. It presents a number of interesting possibilities for modifying the alkyl chain of fatty acids. Olefin metathesis is catalyzed by transition metals like molybdenum (Mo), tungsten (W), and rhenium (Re) (Banks and Bailey, 1964). Metathesis reactions are applied in the petrochemical industry on large scale to vary the olefin chain lengths. A fundamental differentiation exists between self metathesis (between the same olefins) and co-metathesis (between two different olefins) (Wagner *et al.*, 2001). Self-metathesis of oleic acid methyl ester using a tungsten (VI) chloride tetraethyltin catalyst system produces 9-octadecene and 1,18-dimethyl-9-octadecenedioate in an equilibrium mixture (Figure 2.5).

$$2\left(H_3C\text{-}(H_2C)_7\text{-}HC{=}CH\text{-}(CH_2)_7\text{-}COOCH_3\right) \underset{\text{Catalyst}}{\overset{-70^{\circ}C}{\rightleftharpoons}} H_3C\text{-}(H_2C)_7\text{-}HC{=}CH\text{-}(CH_2)_7\text{-}CH_3 + H_3COOC\text{-}(H_2C)_7\text{-}HC{=}CH\text{-}(CH_2)_7\text{-}COOCH_3$$

Figure 2.5: Self metathesis of oleic acid methyl ester

The co-metathesis of erucic acid or oleic acid methyl ester with short-chain olefins such as ethene (ethenolysis) or 2-butene produces unsaturated fatty acid methyl esters of chain lengths C_{10}–C_{15} and the corresponding olefins (Figure 2.6).

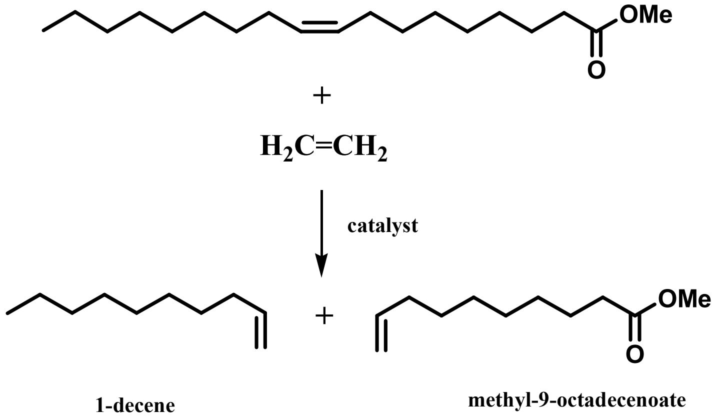


Figure 2.6: Co-metathesis of oleic acid methyl ester and ethene

Diels-Alder and Ene-reactions

Double unsaturated fatty acids like linoleic acid undergo, after isomerization to the fat with conjugated double bonds, Diels-Alder reactions with suitable substituted di-enophiles. Isomerized linoleic acid adds at 100°C to maleic anhydride, fumaric acid, acrylic acid and other di-enophiles with activated double bonds (Danzig *et al.* 1957; Teeter *et al.*, 1957) as shown in Figure 2.7. For the Diels-Alder reaction, the conjugated double bond must be in configuration *trans*/*trans*, which can be achieved via an isomerization catalyst like iodine or sulphur.

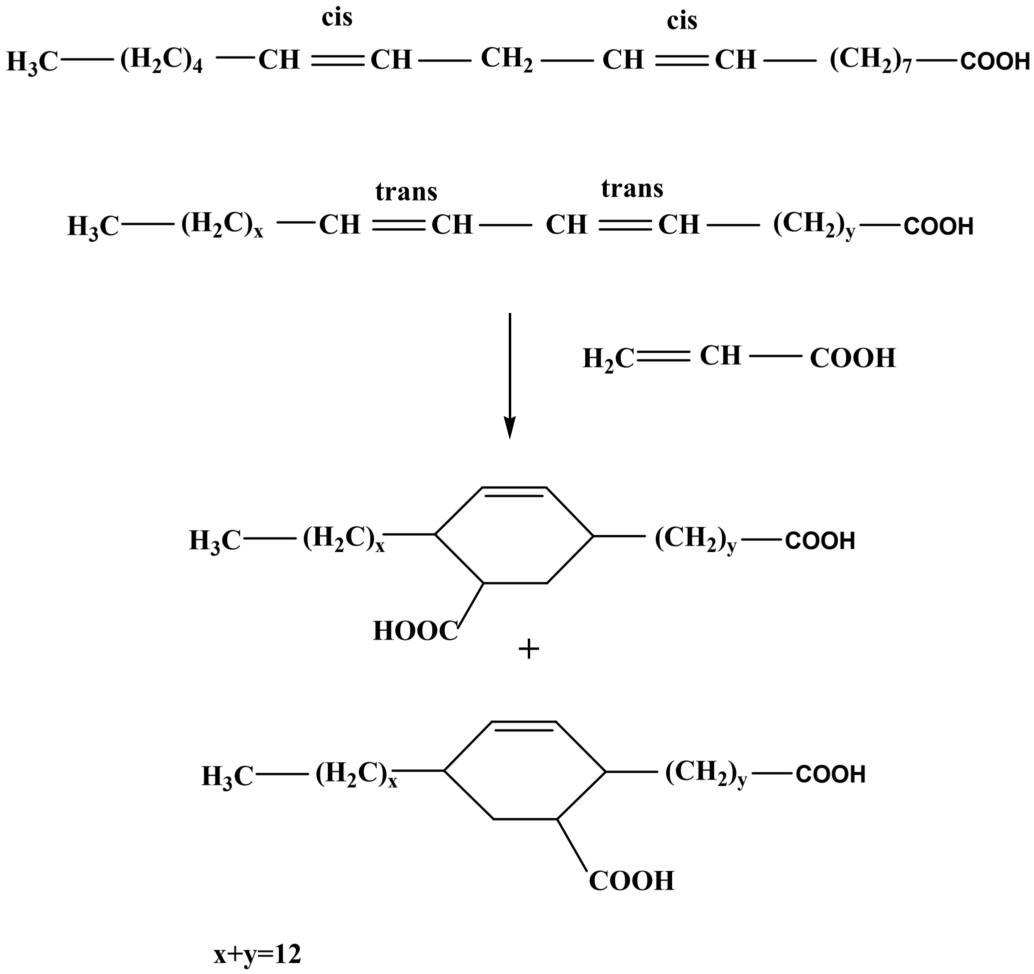


Figure 2.7: Diels-Alder reaction of isomerized (conjugated) linoleic acid with acrylic acid

Unsaturated fatty acids like oleic acid can undergo an Ene-reaction with maleic anhydride or other compound with activated double bonds (Holenberg, 1982) as presented in Figure 2.8.

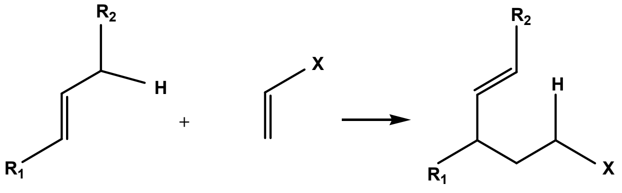


Figure 2.8: Ene-reaction Carboxylation

There are three reactions for the addition of carbon monoxide to the double bonds of fats: hydroformylation (Mullen, 1980) (oxo-synthesis), hydrocarbonylation (Roe and Swern, 1960; Frankel and Pryde, 1977) and Koch synthesis (Melikyan, 1993). These reactions are depicted in Figure 2.9.

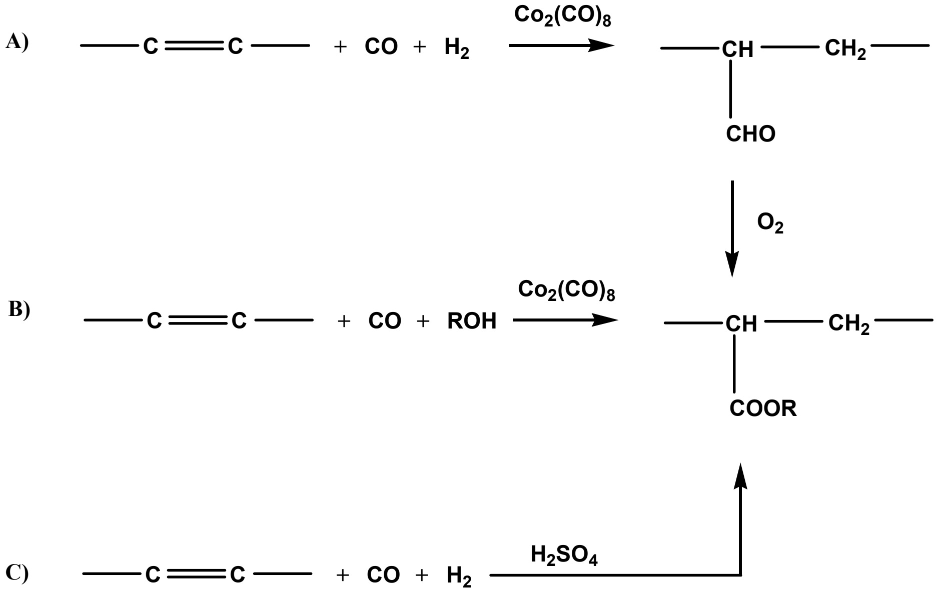


Figure 2.9: Carboxylation reactions on fats: A) hydroformylation with oxidation, B) hydrocarbonylation, C) Koch reaction

Hydroformylation with transition metals builds the formyl group, which can be oxidized to a carboxy group or hydrogenated to a primary alcohol. In protic solvents, like water or methanol, the carbon monoxide is added as carboxy function. Hydroformylation and hydrocarboxylation are catalyzed by di-cobalt octacarbonyl ($Co_2(CO)_8$) and carbonyl-hydride compounds of metals from the 8th group.

Radical additions

Short branches can be introduced by addition of electrophilic radicals to the double bond thus forming functionalized and branched fatty acids and their derivatives. An example of this type of reaction is the radical addition of acetone to oleic acid methyl ester. This reaction is catalysed by manganese (III)-acetate. First, an acetonyl radical is formed, which afterwards adds to the regioisomers 9-(10)-acetonyl stearic acid methyl ester (Figure 2.10). The product mixture yield is up to 72% (Metzger and Riedner, 1989; Metzger and Linker, 1991). Following manganese (III)-acetate initiation, further enolisable compounds such as acetic acid and malonic acid were added to fatty substances (Biermann *et al.*, 2000). Alkanes can be added to olefins in a reaction called an-reaction (Metzger *et al.*, 1981). This reaction is the thermally initiated radical addition of alkanes to alkenes using temperatures of 200-450°C and pressures of 200-250 bar.

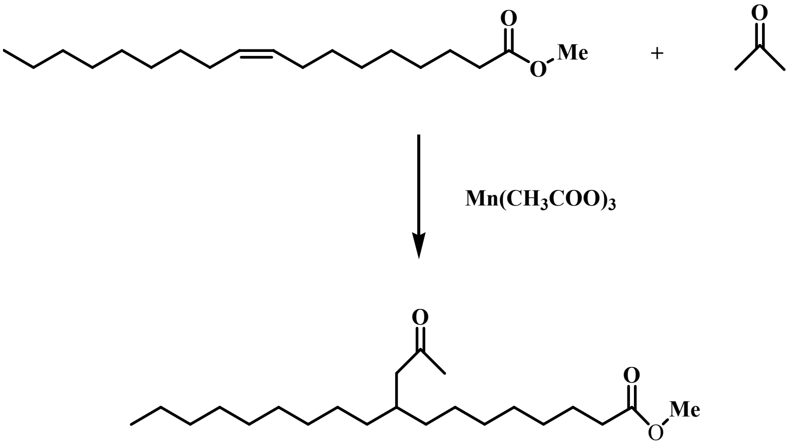


Figure 2.10: Radical addition of acetone to oleic acid methyl ester

Addition of carboxylic acids

Heterogeneously catalyzed addition of carboxylic acids to the un-saturation of vegetable oils was successfully undertaken and the reactions are currently being scaled-up to evaluate the lubricant properties of the products (Hölderich, 2001). The addition of formic, acetic and pivalic acid to methyl oleate was carried out using nafion/silica composite catalysts (Fischer and Hölderich, 2000) (Figure 2.11). This modification and the use of sterically hindered acids, improves the hydrolytic and oxidation stability of the fatty substances, which is the reason why neoacids are often used. The best yields obtained were 80% for the addition of formic acid, 52% for the addition of acetic acid and 41 % for the addition of pivalic acid. The heterogeneously catalyzed addition of carboxylic acids to the epoxidized oils, producing vicinal hydroxy-esters, is currently being studied. Using the epoxide, as intermediate for these reactions, is advantageous because milder reactions conditions are required amid the higher reactivity of the epoxide ring compared to that of the double bond.

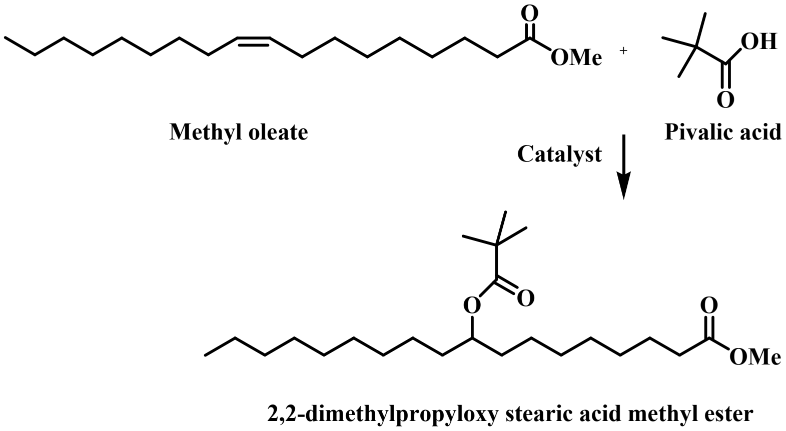


Figure 2.11: Addition of pivalic acid to methyl oleate over solid acid catalysts

Dimerization (dimer acids and estolides)

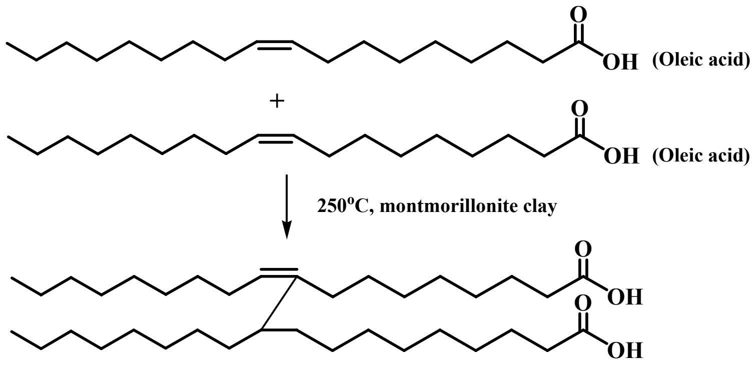
Dimerization of unsaturated fatty acids occurs in the presence of radical sources, by heating at temperatures between 260ºC and 400ºC and under the influence of clay or other cationic catalysts (Gunstone, 1999). The last procedure is used on a commercial basis to meet the demand for dimer acids. Typical manufacturing conditions use a montmorillonite clay catalyst (4%) at 230ºC for 4-8 hours followed by distillation to produce a dimer concentrate, which contain some trimer.

Dimerization is usually carried out in the presence of a little water (1-2%). If this is increased, (9-10%) a new product (mono-estolide) is produced in useful yield. These are interesting substances with structures similar to that given in Figure 2.12 (Gunstone, 1999).

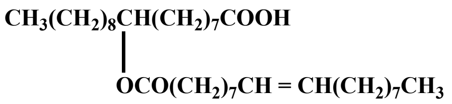
Epoxidation

Epoxidation is one of the most important double bond addition reactions. In the case of unsaturated fatty acid esters, it is often performed *in situ* using the performic acid method (Figure 2.13). This process is industrially performed on a large scale (Bauman *et al.*, 1988).

At present, the vegetable oil epoxides are used in PVC and stabilisers (*Wagner et al.*, 2001). Furthermore, they are also used to improve the lubricity in lubricants. Because of their good lubricity and high oxidation stability in comparison to rapeseed oil, pure epoxidized rapeseed oil can also be used as a lubricant base fluid (Wu *et al.*, 2000). Epoxidised fatty components are reactive substrates for a number of interesting products. Ring opening of such epoxidised oils with organic acids or alcohols produce epoxy polyol esters and epoxy polyethers. These are widely used in polymer chemistry, e.g. in the areas of paints and dyes. The cleavage of the epoxy ring allows also the introduction of hetero-atoms and a whole series of functional groups (Baumann *et al.*, 1988; Pavlovicová and Cvengroš, 1999). Thus, a whole new series of oleochemical products can be manufactured, which can be used as lubricant base fluids, additives, etc.



(a)



$$\begin{array}{l} CH_3(CH_2)_8CH(CH_2)_7COOH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OCO(CH_2)_7CH = CH(CH_2)_7CH_3 \end{array}$$

(b)

Figure 2.12: a) Dimer acid, b) A typical mono-estolide.

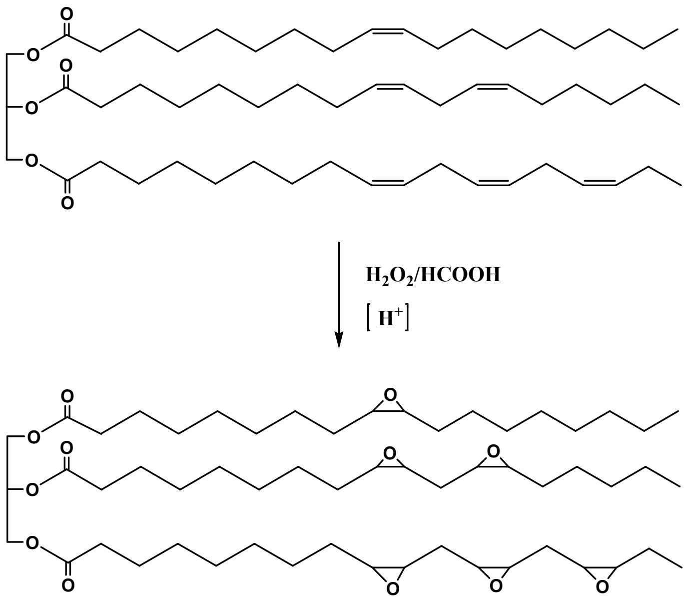


Figure 2.13: Epoxidation Reaction of Vegetable Oils (Wagner *et al.*, 2001)

b) Reactions at the Carboxyl Groups

Transesterification

Transesterification is the process of using an alcohol (e.g., methanol or ethanol) in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to chemically break the molecule of the raw vegetable oil into their methyl or ethyl esters with glycerol as a by-product. A large number of transesterifications have been reported with lower alcohols such as methanol, ethanol, and isopropanol to obtain esters of commercial applications for use as biodiesel, plasticizer solvent, cosmetic base fluids, and lubricants (Anand *et al*; 1998). Few transesterification reactions are reported with higher alcohols C8 to C14, for use as lubricants. However, glycerol is not desired in triacylglycerol structure because of the presence of one H atom on the carbon atom in the β-position of ester groups; this make esters more susceptible to elimination reaction leading to subsequent degradation of the molecule. The low stability of glycerol β-carbon may be eliminated by transesterification using more resistant polyhydric alcohols with a neopentyl structure without hydrogen at β-carbon, such as isosorbitol or neopentylpolyols, including pentaerythritol (PE), trimethylolpropane (TMP), or neopentylglycol (NPG) (Figure 2.14) for utilizing the transesterified products as lubricant base material (Birova and Cvengros,2002; Uosukainen *et al*; 1998; Bondioli *et al*; 1999).

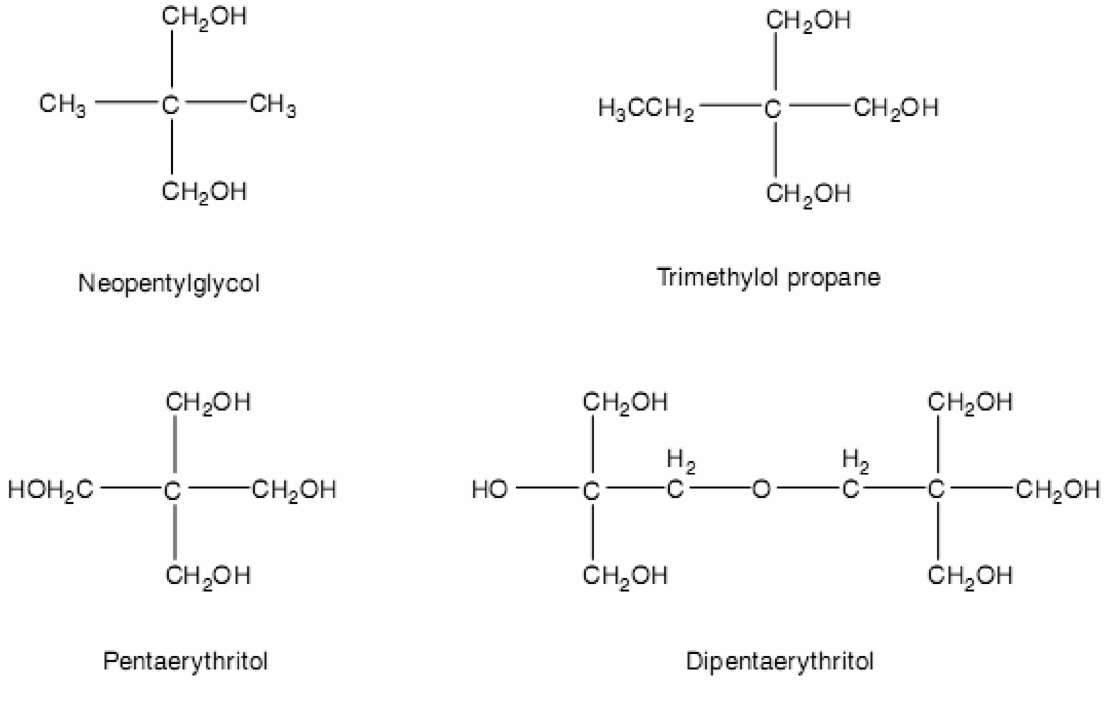


Figure 2.14: Examples of polyols used for transesterified vegetable oil based lubricants(Erhan *et al*; 2006)

Sodium alkoxide of the corresponding alcohol acts as best catalysts for transesterification with yields of monoesters ranging from 80 to 90% (Figure 2.15). Linseed has been transesterified with polyethylene glycol (molecular weight 300) using Na_2CO_3 as a catalyst at 210◦C. Sodium can be used as catalyst instead of NaOH or Na_2CO_3. Sulfuric acid is used for ring opening reaction at the epoxy group in epoxidized soybean oil followed by transesterification at the ester group (Hwang *et al*; 2003). Some other catalysts systems are shown in Figure 2.16. Most of the esters of higher alcohols have been prepared in a two-step process. In the first step, vegetable oil is hydrolyzed to corresponding fatty acids by a variety of methods. Most common being hydrolysis by steam (Sonntag, 1982) in continuously operating reaction columns at 250◦C and pressures between 2×106 and 6×106 Pa (20 to 60 bar). In the counter current flow method, the glycerol that is formed is extracted continuously from the equilibrium mixture using water, yielding 98% hydrolysis in a single pass, without any catalyst. Other methods use acid hydrolysis at elevated temperature with hydrochloric or mixtures of sulfuric acid and sulfonic acid. Alkaline hydrolysis (saponification) of vegetable oils yield alkali soaps and glycerol, and is now of minor importance. The fatty acids are then esterified in the second step with corresponding alcohol using sodium alkoxide formed in situ and p-toluene sulfonic acid/sulfonic acids and cation exchange resins as catalysts. Simultaneous transesterification and saponification of castor oil has been utilized to prepare completely vegetable oil based greases (Dwivedi *et al*., 2002). The alkali used as a catalyst for transesterification reaction serves as a reactant for the saponification reaction. The use of appropriate proportions of oil, alcohol, and alkali will thus form grease with desired composition and properties. Various commercial processes for producing alkyl esters, useful in bio-fuels and lubricants, are available. The alkali catalyzed transesterification of vegetable oils with methanol to give fatty acid methyl esters and glycerol

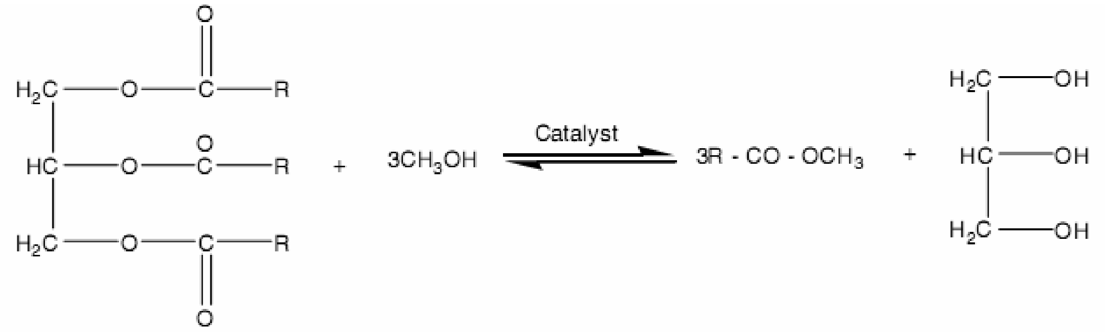


Figure 2.15: Transesterification with methanol(Erhan *et al*; 2006)

Transesterification of glycerides or esterification of free fatty acids is conducted in a single critical phase medium or increased reaction rates, decreased loss of catalyst or catalyst activity, and improved overall yield of the desired product (Ginosar and Fox, 2000). In this method, glycerides or free fatty acids in vegetable oils and restaurant grease are mixed with an alcohol stream or water streamand dissolved in a critical fluidmedium, reacting the mixture in a reactor over either a solid or liquidacidic or basic catalyst. The product stream is separated from the critical fluid medium in a separator, where the critical fluid medium can be recycled to the process. Transesterification reactions of the partially hydrogenated and cyclized ester vegetable oils are important because these reactions yield monoesters of vegetable oils with better thermal stability and lower freezing points than the vegetable oils as such.

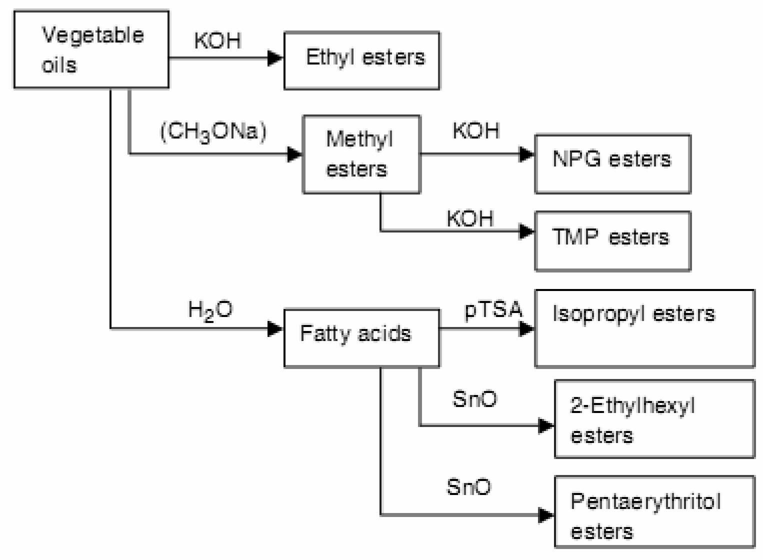


Figure 2.16: Different transesterification routes (Erhan *et al* ,2006)

Hydrogenation

Some vegetable oils such as linseed oil and rapeseed oil have a high degree of unsaturation depending on the amount of linoleic and linolenic acid derivatives. As a result, the thermo-oxidative stability of these oils is poor and leads to polymerization resulting in gummy and resinous products at elevated temperatures. Their use as lubricants with out reduction of unsaturation can cause deposit formation, corrosive action, and damage with relatively short useful service life. One of the several ways to reduce unsaturation is to partially hydrogenate and cyclize these vegetable oils to improve their service lives without affecting the freezing points to a large extent. Complete hydrogenation used in industry with nickel catalyst is not desired, as it affects the low temperature properties. The problem of achieving selective hydrogenation has so far been only partly solved. An example is the conversion of linolenic and linoleic to oleic acid without unwanted positional or cis–trans isomerizations occurring at the same time. Even the use of heterogeneousmetal catalysts, which are preferred in technical processes, have not yet led to satisfactory results (Draguez and Demoulin, 1984). Partial hydrogenation of cottonseed oil has been demonstrated using chromium-modified nickel catalyst (Krishnaiah, and Sarkar, 1990). Chromia has been found to suppress the stearate formation completely, although it retarded the overall hydrogenation activity of the nickel catalyst. Homogeneous catalysts based on complexes of precious metals could offer a solution to the problem, if a method could be found for recovering and recycling these expensive catalysts.

2.3 Lubricants and the Environment

Awareness of the adverse impact of mineral oil based lubricants has forced the lubricant industry to increase the ecological friendliness of its products. Increasing attention to the environmental issues and more restrictive environmental regulations has forced the lubricant manufacturers to increase the biodegradability of their products. In general biodegradability means the tendency of a lubricant to be ingested and metabolized by micro-organisms. The rate at which lubricants, and other chemicals or additive components, biodegrade is related to their chemical structure. Their chemical structure affects their properties, many of which affect performance in the various tests for biodegradability.

Vegetable oils are candidates for replacement of mineral oils due to their inherent biodegradability, non-toxicity, and excellent lubricity (Adhvaryu *et al.*, 2005). Additionally, vegetable oils are from renewable resource, and their cost is reasonable compared with that of other alternative biodegradable fluids. Volumes of lubricants, especially engine oils and hydraulic fluids, are relatively large and most of them are based on mineral oils. Lubricants based on vegetable oils still comprise a narrow segment. However, they are finding their way into applications such as chainsaw bar lubricants, drilling fluids and oils, straight metalworking fluids, food industry lubricants, open gear oils, biodegradable grease, hydraulic fluids, marine oils, outboard engine lubricants, oils for water and underground pumps, rail flange lubricants, shock absorber lubricants, tractor oils, agricultural equipment lubricants, elevator oils, mould release oils, and two-stroke engine lubricants (Erhan and Asadaukas, 2000).

Recently, environmental behaviour of lubricants such as biodegradability, toxicity, water hazard potential, and emissions has received much attention (Goyan *et al.*, 1998). Hence, these aspects of vegetable oil based lubricants are briefly reviewed. Release of lubricants in to marine environment and subsequent damage to aquatic life has also been a subject of much concern (Mercurio *et al.*, 2004) and hence a brief review of hydrocarbon degradation in marine environment is included.

Any product can be classified in terms of their environment impact as:

1. Environment friendly (improving environment)
2. Environmentally neutral (harmless to nature)
3. Environment impairing (causing damage to environment)

A lubricant at best can only be environmentally neutral. A lubricant is considered environmentally acceptable if it meets the following requirements (Bartz, 1998; Bartz, 2006).

1. At production, the lubricant should be environmentally neutral; consume low energy; produce no waste materials; produce no emission.
2. If possible, the lubricant should be from renewable source; there should be no depletion of resources; no net addition to the greenhouse effect.
3. The lubricant should be physiologically harmless, non-toxic, and non-cancerous.
4. No toxic decomposition substances; non bio-accumulative potential
5. The lubricant should be eco-toxicologically acceptable; non-water endangering; non-water miscible; have lower density than water.
6. The lubricants should have fast biological degradability and should not produce any toxic or unpleasant decomposition products.
7. The lubricant should not cause any disposal problems; should be easily recyclable.

2.3.1 Biodegradability

By more readily biodegradable it is meant that the fluids, using standard methods and processes, are converted from the lubricating fluids to lower molecular weight components that have essentially no environmental impact. The rate at which lubricants, and other chemicals or additive components, biodegrade is related to their chemical structure. Hydrocarbons are broken down into carbon dioxide and water by naturally occurring bacteria in soil and water. Since biodegradability is environment dependent, substances which readily degrade under one set of conditions may persist under others. In order for biodegradation to occur, there must be sufficient bacterial population, adequate oxygen, and suitable ambient temperature. The source of food for the bacteria is the oil itself, but an excess of oxygen must be present for a reasonable rate of biodegradation to take place (Goyan *et al.*, 1998). Complete biodegradability indicates the lubricant has essentially returned to nature. Partial biodegradability usually indicates one or more component of the lubricant is not degradable. The extent of biodegradability is affected by the following (Kitamura, 1993):

- Biological constituents (hydrocarbons, amino acids, fatty acids s, etc.) are generally readily biodegradable.
- Aromatic compounds are generally resistant to biodegra dation; a benzene ring possessing –OH, –COOH, –NH2,–CH, –CH3, or –OCH3 is rather easily biodegraded, but structures possessing –X (halogen), –NO2, and –SO3H are resistant to biodegradation.

- Biodegradation of linear hydrocarbon compounds occurs more readily than branched hydrocarbon compounds. For example, erucic acid estolides, which are branched structures, degrade 84% compared to erucic acid, which degrades to 98**%** (Erhan and Kleiman, 1997**)**. Biodegradability changes with the position and degree of chain branching.
- Sterically hindered ester linkages in chemically modified vegetable oils, decreases the biodegradability to a greater extent.
- Biodegradability of transesterified vegetable oils products decreases with the length of the acyl and alcohol chains.

Readily biodegradable is defined as degrading 80% in saltwater within 21 days. Most of the bio based hydraulic fluids are readily biodegradable. Inherently biodegradable are typically food-grade lubricants and white mineral oils and takes longer than vegetable oils to degrade in the environment and are toxic over long periods. Several testing methods have been developed to evaluate the biodegradability of the base fluids as well as of the additives of the lubricant. The following test methods are widely used to evaluate the biodegradability of lubricants.

1. CEC decomposition test CEC-L-33-A-94 (1994)
2. Zahn-Wellens-Test OECD 302B (1992).

2.3.2 Toxicity

Environmentally neutral fluids must be not only biodegradable but non toxic as well such that they shall not harm flora and fauna. Toxicity tests are used to determine the effect of a compound on the flora and fauna in the environment. The result is quoted as LD_{50}, the dosage (lethal dosage) which will cause mortality or severely hinder growth of 50% of the population (Goyan *et al.*, 1998).

Regarding eco-toxicity, a general rule of thumb exists, according to which materials with an LD_{50} value > 1000 ppm are low or non-toxic. In fact ecotoxicity represents the toxic effect of a lubricant on plants and animals (not on human health) (Bartz, 1998). Toxicological properties of fully formulated lubricants are related to those of the base oil and additive components. Measured toxicity of mixtures is generally found to be close to the arithmetic sum of component toxicities. Due to contamination by fuel and combustion products, the toxicity of used lubricants may be significantly different from that of fresh oils. The most useful general information on the toxicological behaviour of base oils can be found in

CONCAWE, 1987. As per the criteria laid out by CONCAWE, vegetable based lubricants are 100% non-toxic.

2.3.3 Water Hazard

As per water hazards criteria environmentally acceptable lubricants require (Bartz, 1998):

1. Water hazard classification = 0
2. Fast biodegradable

The water hazard classification is calculated using three evaluation numbers for the acute oval mammalian toxicity, acute bacteria toxicity, and acute fish toxicity. According to German standard for water hazard classification, vegetable oils are classified as not water endangering (WGK 0) (Bartz, 1998) as given in Table 2.3.

Table 2.3: Water Hazard classification of lubrication oils (Bartz, 1998)

WGK 0	No water endangering	Vegetable oils
WGK 1	Low water endangering	Plain lubricating oils, base oils, and white oils
WGK 2	Water endangering	Additivated lubricating oils, engine and industrial oils
WGK 3	High water endangering	Additivated water miscible lubricating oils, water miscible coolants

Studies conducted by Australian Institute of Marine Science (AIMS) demonstrate vegetable oil lubricants biodegrade significantly faster under tropical marine conditions than their mineral oil counterparts (Mercurio *et al.*, 2004). The scientific study is a world first in the tropical marine environment and was a collaborative partnership between Australian Institute of Marine Science (AIMS) and the Fuchs Lubricants (Australasia), which specializes in lubricants for a diverse range of applications. The study was conducted in seawater over 7 and 14-day periods using natural mangrove and coral reef microbial communities. Over 14 days, the reef microbes degraded the vegetable oil lubricant by 55% and the mangrove microbes degraded the vegetable oil based lubricant by 71%. Both reef and mangrove micro-organisms failed to significantly degrade the two-stroke mineral oil lubricant over 14 days (Mercurio *et al.*, 2004).

2.4 Physio -Chemical Properties of Vegetable Oils

Vegetable oils are very good boundary lubricant in that they give rise to very low coefficient of friction (μ). At the same time, many researchers report that even while the coefficient of friction is low with vegetable oil as a boundary lubricant, the wear rate is high (Bowden and Tabor, 2001). It is possible that this behaviour is due to the chemical attack of the surface by the fatty acid. On this view, the metallic soap film is rubbed away during sliding and is continuously reformed by further chemical reaction. Non-reactive detergents may also produce a similar increase in wear and suggests that the additive removes, by a detergent action, the detritus on the surface, which otherwise would act as a protective film (Bowden and Tabor, 2001).

Studies reported in Bisht *et al.*(1993), Gapinsky *et al.* (1994), Asadauskas *et al.* (1996), Asadauskas *et al.*(1997), and Goyan *et al.* (1998) show that vegetable oils have excellent properties relating to friction and wear when used as base stocks or as additives. These papers used various vegetable oils in their tests like castor oil, sunflower oil (high oleic), and jojoba oil. More recently Kržan and Vižintin (2003) have shown that lubricant formulations with rapeseed oil and high oleic sunflower oil as base oil have superior tribological performance than a mineral oil based formulation.

Goyan *et al.* (1998) used tribological tests (four ball), to evaluate the wear scars and values of coefficient of friction for rape seed oil (with major fatty acids C20:1, n-9 and C22:1, n-9), sunflower oil (oleic, linoleic and linolenic), castor oil (ricinoleic) and two mono-esters of oleic acid. They concluded that chemical structure differences affect wear and friction. Among all the oils tested mono-esters of oleic acid showed the best results followed by rapeseed oil (with longer hydrocarbon chains C20:1, n-9 and C22:1, n-9). Tests were performed with and without antiwear additives. Poly-unsaturation of sunflower oil led to an unexpectedly higher wear, whereas the hydroxyl group branching of castor oil did not show any effect due to additive interaction. The studies conclusively showed that chain length and un-saturation of the constituent fatty acids have an effect on the friction and wear properties of vegetable oils. Un-saturation in vegetable oils led to interaction with additives affecting the tribological performance. Coconut oil with low un-saturation (<10%) is expected to be less prone to deleterious interaction with additives.

A summary of some of the important lubricant-related properties of vegetable oils has been recently published that compares these properties with those of synthetic esters and poly alpha olefin lubricants (Rudnick *et al*; 2002). Detailed physical property data for many of the common vegetable oils, including American Society for Testing of Materials (ASTM) test results, have been reported by Lavate *et al*; .1997.

2.4.1 Viscosity and Viscosity Index

The viscosity of lubricating oils is one of their most important properties when specifying an oil for a particular application. The chemical structure of the vegetable oil affects the flow properties of the oil. For example, if a fluid oil that contains a significant quantity of oleic, linoleic, or linolenic acids or other unsaturated components is hydrogenated to produce a saturated version, the new material would have the properties of grease (Rudnick and Erhan, 2006). The viscometric behaviour of fluids is characterized by viscosity, viscosity index, low temperature fluidity, and compressibility. The viscosity–temperature dependence of chemically modified vegetable oils is more favourable, with the viscosity index approaching 200. Other reactions such as oxidation, polymerization, or oligomerization also enable the production of lubricants with wide viscosity range (10 to 10,000 cSt at 40◦C). Besides the oxidation and oligomerization, an increase in viscosity can also be achieved by changing the chain length of the acyls and through branching. Viscosity increases with increase in acyl chain length. In isolated acyls, branching results in a viscosity decrease (Hwang *et al*; 2003) however, viscosity increases if cross-linking occurs in branched acyls. Cross-linking may occur via carbon, ether, or sulphide bonds.

Table 2.4: Effect of Fatty acid unsaturation, chain length and branching on properties of base fluids (Hwang *et al*; 2003)

	Lubricity	VI	Low Temperature Fluidity	Oxidative Stability	Volatility
Chain Length	++	+	_	_	+
Chain Branching	_ _	_ _	+	+	_
Unsaturation	_	+/-	+	_ _	+/-

++very positive effect; +positive effect; +/- without effect; - - very negative effect

Viscosity also increases on increasing the molecular weight and chain length of the alcohol. Viscosity of vegetable oils can be lowered by blending with biodegradable synthetic fluids such as adipates, oleates, poly alpha olefins, and mineral oils for desired applications (Erhan and Adhvaryu, 2002). Viscosity index increases with increasing fatty acid and alcohol chain length used for vegetable oil transesterification (Erhan *et al*;2006) It decreases with the introduction of branching and cyclic groups in chemically modified vegetable oils, resulting in a more compact molecular configuration.

2.4.2 Oxidation Stability

Vegetable oils especially poly-unsaturated oils are known to possess low oxidative stability (Zeman *et al.*, 1995; Adhvaryu and Erhan, 2002). The properties of vegetable oils are determined by their fatty acid composition. A high content of linoleic/linolenic acid decreases thermal and oxidative stabilities. The relative rates of oxidation of oleic acid, linoleic acid, and linolenic acids are 1, 10, and 100, respectively (Rudnick and Erhan, 2006).

Fundamental knowledge of the oxidative properties of lubricants is necessary to predict the long-term thermal stability of these fluids, which is a critically important lubricant property. Oxidation properties evaluated experimentally are often used to predict actual lubricant service life in high temperature and other extreme applications. The more resistant a lubricant is to oxidation, less is the tendency it has to form deposits, sludge, and corrosive by-products in grease, engine oil and industrial oil applications. It is also more resistant to undesirable viscosity increases during use. Igarashi (1990) has discussed various chemical reaction mechanisms based on free radicals, which are thought to be involved in the oxidative degradation of engine oils. The ASTM D943 test method is very widely used in industry to assess storage and long-term service oxidation stability of oils in the presence of oxygen, water, copper and iron at an elevated temperature (95 °C).

In developing new lubricants, it is not usually possible to screen a large number of base oils and anti-oxidant quantity by running expensive and time-consuming performance tests using mechanical hardware. For these reasons, it has become necessary to seek development of new oxidation stability tests, which are capable of representing field performance within a short testing time. Actually, thermoanalytical methods such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have received considerable attention (Dweck and Sampaio, 2004; Santos *et al.*, 2004). These methods are advantageous in relation to the conventional ones because they provide a higher precision and sensitivity as well as use smaller amount of sample and the results are obtained faster.

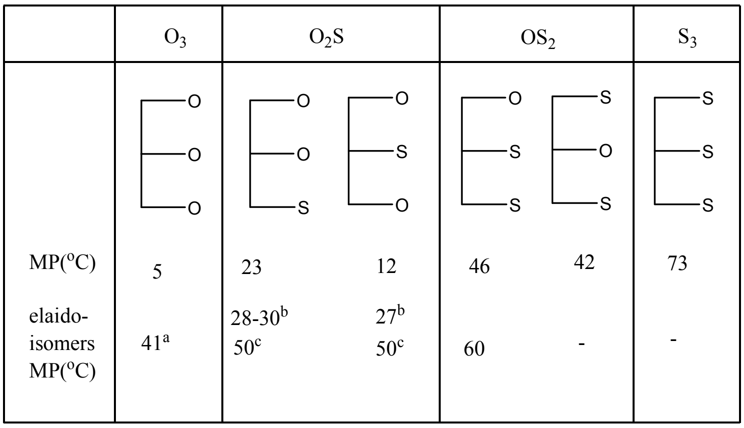
Thermogravimetric analysis (TGA) provides the analyst with a quantitative measurement of any change associated with a transition. For example, TGA can directly record the loss in weight with time or temperature due to dehydration and decomposition. Thermogravimetric traces (thermograms) are characteristic for a given compound or system because of the unique sequence of physicochemical reactions that occur over definite temperature ranges and at rates that are a function of molecular structure (Merrit and Settle, 1986). Changes in weight are a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to evolution of volatile products or the formation of heavier reaction products. In differential thermal analysis (DTA), the temperature of a sample and a thermally inert material are measured as a function of temperature (usually sample temperature). Any transition which the sample undergoes will result in liberation or absorption of energy by the sample with corresponding deviation of its temperature from the reference. The differential temperature (ΔT) versus the programmed temperature (T) at which the whole system is being changed tells the analyst of the temperature of transitions and whether the transition is exothermic or endothermic. In isothermal TGA/DTA, the reference temperature remains constant whereas the sample temperature varies according the thermal activities occurring in it.

Most of vegetable oils are triglyceride esters (triacylglycerols) of different fatty acids with a very few exceptions like jojoba oil (Gunstone, 1999). They are, therefore, complex molecules with different fatty acids attached to a single triglyceride structure. The presence of unsaturation in the triacylglycerols molecule due to C=C from oleic, linoleic and linolenic acid moieties, provides many active sites for various oxidation reactions. Saturated fatty acids have relatively high oxidation stability (Brodnitz, 1968)**,** which decreases with increasing unsaturation in the molecule. Unsaturated oils react with oxygen through a free radical process to form hydroperoxides, which in turn decompose and then crosslink to form polymeric gels. This process is called autoxidation and has been covered thoroughly in reviews (Russell, 1959; Porter *et al.*, 1995). Weight changes are a measurable and an inevitable consequence of the autoxidation processes. Oxygen uptake increases the weight of the oil, as hydroperoxides are formed while bond cleavage produces volatile oxidation by-products such as carbon dioxide, and short chain acids, aldehydes, ketones, and alcohols. These diffuse out, volatilize, and decrease the weight (Hancock and Leeves, 1989). The measured weight changes represent the net change in weight of the oil film due to oxygen uptake during the free radical and polymerization process and the diffusion and loss of volatiles created by oxidation and molecular rearrangements.

Rates of vegetable oxidation are directly related to the type and amount of un-saturation present in the fatty acids of the vegetable oil. Vegetable oils, in general, are less volatile than isoviscous mineral oils and synthetics. Also hydrocarbon oxidation rates are dependent on temperature, surface contact with metals, and irradiation sources such as sunlight or UV light (Rasberger, 1997). The autoxidation process is known to involve free radicals, and therefore, approaches taken to retard the process of oxidation utilize free radical chain-breaking antioxidants (primary antioxidants) and hydroperoxide decomposers (secondary antioxidants) and combinations of both of these classes of antioxidants. The details of the application of antioxidants in the field of lubrication have been recently reviewed (Migdal, 2003).Vegetable oil oxidation has been described in terms of primary and secondary stages by Fox and Stachowiak (2003). The first stage involves the free-radical formation of hydroperoxides on the fatty acid portions of the molecule, while in the second stage, after sufficient buildup of the hydroperoxide concentration, there is decomposition to form alcohols, aldehydes, and ketones along with volatile decomposition products.

2.4.3 Cold flow properties of Vegetable oils

Vegetable oils are not pure organic compounds with sharp melting point but mixtures so that at any given temperature the sample may be wholly solid, wholly liquid, or frequently a mixture of solid and liquid (Gunstone, 1999). In the solid state, long-chain compounds exist in more than one crystalline form and consequently have more than one melting point. The melting points of triacylglycerols depend not only on chain length but also on the nature of the un-saturation (*cis*- or *trans*-olefinic) and on the number and relative position of the unsaturated centres.



	O_3	O_2S		OS_2		S_3
	O O O	O O S	O S O	O S S	S O S	S S S
MP(°C)	5	23	12	46	42	73
elaido-isomers MP(°C)	41[a]	28-30[b] 50[c]	27[b] 50[c]	60	-	-

[a]trielaidoester(E_3)
[b]monoelaidoester(EOS)
[c]dielaidoesters(E_2S)

Figure 2.17: The effect of fatty acid constituents and the nature of unsaturation on the melting points of triacylglycerols (S- stearic acid, O- oleic acid, and E- elaidic acid)

The effect of fatty acid constituents and the nature of un-saturation on the melting points of triacylglycerols is depicted in Figure 2.17 (Gunstone 1999). It has been known that fats, unlike most other organic compounds, show multiple melting points. Glycerol tristearate was reported to have three melting points (Gunstone, 1999). X-ray powder diffraction studies confirmed three crystalline forms, namely α (hexagonal subcell), β' (orthogonal subcell), and β (triclinic subcell) (Sato, 2001). When the melt of a simple triacylglycerol is cooled quickly it solidifies in the lowest melting form (α) which has perpendicular alkyl chains (i.e. the angle of tilt is 90°). When heated slowly this melts and held just above the α melting point, it will resolidify in the β' crystalline form. The β form has the highest melting form and is produced also by crystallization from solvent. The series of changes is shown by the sequence in Figure 2.18 (Marangoni, 2002):

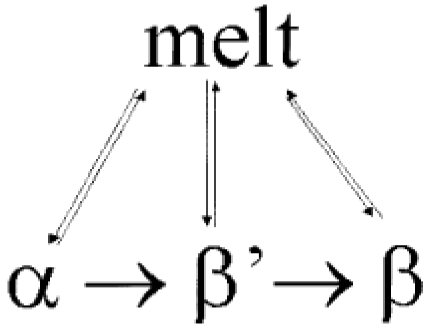


Figure 2.18: Polymorphism in fat crystallization

Mono-acid triacylglycerols show three distinct melting points corresponding to the three crystalline forms as shown above (Lutton and Fehl, 1970; Hagemann and Rothfus, 1983). In some mixed triacylglycerols, no β form is present and such compounds have highest-melting β' form (Sato, 2001).

Crystallization kinetics generally is very sensitive to temperature fluctuations and related factors such as cooling rate or thermal history. As can be expected from nucleation theory and crystallization thermodynamics, presence of contaminants, foreign bodies, or other nucleation centres and even shaking may affect crystallization. Since solidification thermodynamics of vegetable oil is exceedingly complex, only indirect semi quantitative data are available from techniques such as cooling the liquid and measuring its viscosity increase, precipitation or loss of fluidity. In the industry one major characteristic of the low-temperature properties of lubricating fluids is pour point (PP). ASTM D97 technique determines it by placing a test tube containing 50 ml, of the sample into a metal cylinder, which is submerged into cooling media, and measuring the temperature at the top of the sample until it stops pouring. The temperature of cooling media is kept constant below the sample temperature. When the sample temperature reaches the specified range (e.g. three of the ranges are +9 to -6, -6 to -24 and -24 to -42°C), the temperature of cooling media is also reduced to the specified value (-18, -33 and -51°C, respectively). The precision statement in the standard (ASTM D97) suggests that the difference between two test results from independent laboratories exceeds 6°C in one case out of 20, and repeatability is 2.87°C at 95% confidence.

The ASTM D97 method alone is inadequate to understand the cold flow properties of a lubricant. There are two major limitations of the pour point test: its rapid cooling rate and its qualitative nature. In ASTM D97 method the measurement is made by placing a sample in a glass cylinder and cooling rapidly at a rate of approximately 0.6°C/minute (Kinker, 2000). This is a fairly rapid cooling rate that may not allow sufficient time for ultimate crystal growth and strength. Vegetable oils used in environmentally acceptable hydraulic fluids often have acceptable ASTM pour points but can solidify at temperatures warmer than the "pour point temperature" upon extended storage time. The qualitative nature of ASTM D97 method does not provide knowledge of fluid viscosity; it is only a determination of the temperature at which flow ceases. Low-temperature studies have shown that most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification much above the pour point upon long term cold storage (Adhvaryu *et al*., 2005; Rhee *et al*., 1995; Kassfeldt and Goran, 1997). At high cooling rate, large proportion of the crystals formed at low temperature is the unstable (α) polymeric form (Cebula and Smith, 1991). Formation of this unstable material is almost absent at slow cooling rates (0.1 ºC/ minute), when only the stable polymeric form (β) was observed.

Efforts have been made to improve the low-temperature properties by blending the vegetable oils with diluents such as poly α olefin, diisodecyl adipate, and oleates (Asadauskas and Erhan, 1999). The effect of diluents and pour point depressants (PPD) on vegetable oils has been unsatisfactory. The other possible way to control these obstacles is structural modification of the oils by chemical reaction (Erhan and Asadauskas, 2000). It has been reported that triacylglycerols with more diverse distribution of fatty acids on the glycerol backbone have lower solidification temperatures (D'Souza *et al*., 1991). Chemical modification of the vegetable oils to give more complex structures should improve the low-temperature properties (Wagner *et al*., 2001).

2.5 Scope of the Present Work

The foregoing discussion shows that widespread use of vegetable oils as lubricant base stocks is precluded mainly by their poor cold flow properties. Saturated oils show excellent oxidative stability and hence are good candidates as base oil for lubricants except that their cold flow properties are unacceptably poor. Two avenues are open for the modification of vegetable oils namely; a) use of appropriate pour point depressants or diluents and b) Chemical modification. The major chemical modification processes are reviewed in Section 2.2.2. Since the fatty acid chains (length and presence and number of double bonds) of the triacylglycerol structure determine the properties of vegetable oils their exchange with appropriate alcohols (transesterification), redistribution among triacylglycerol molecules (interesterification) or modification (reactions at the double bond site) can bring about considerable change in their properties. Saturated fatty acids have straight chains (linear conformation) which are detrimental to cold flow behaviour. The double bonds in mono- and poly-unsaturated have bent conformations and are good for better cold flow behaviour but they lead to poor oxidative stability. Cold flow properties can be improved by preventing the formation of large crystal structures by using appropriate PPD which co-crystallizes with triacylglycerol molecules. Another method is to add side chains at double bond sites by appropriate chemical reactions. The latter method has the advantage of eliminating the un-saturation in fatty acid chains whereby improving oxidation stability. The present work envisages the implementation of the above methods to improve the cold flow properties of vegetable oils especially saturated vegetable oils which are know to have very poor cold flow properties. Being a saturated vegetable oil with a high pour point of 24 ºC and abundantly available in the tropical area, coconut oil has been used in this work for the analysis and improvement of its cold flow properties using the methods suggested in the literature survey.

Chapter 3

Analysis of Pour Point of Vegetable Oils and Effect of Additives on Vegetable Oils by DSC

3.1 Introduction

Pour point depressants (PPD) have been created to suppress formation of large crystals during solidification, although the mechanism of PPD action on triacylglycerol crystallization remains undisclosed (Acryloid, 1995). Typically, commercial PPD are known to contain a polymethacrylate backbone with a certain type of branching, which allows inclusion of the PPD molecule into the growing crystal. However, vegetable oil containing PPD have still shown unsatisfactory performance when exposed to low temperatures for durations significantly longer than those specified in ASTM D97 test (Rhee *et al.*, 1995). For the purposes of producing biodegradable lubricants with improved low-temperature performance, various diluents are often added to vegetable oils (Kassfeldt and Goran, 1997). Lack of fundamental knowledge on crystallization of mixed acid triacylglycerols does not permit more accurate prediction of the pour point and other low-temperature properties. Dilution with petroleum products may reduce the PP (Dunn and. Bagby, 1995) to a limited extent. It is still unclear whether other diluents can demonstrate this effect as well. Synthetic diesters and polyol esters (Randles and Wright, 1992; Battersby *et al.*, 1992, PAO (Carpenter,1995; Carpenter,1994), and oleates (van der Waal and. Kenbeek,1993) have typically been employed as diluents in biodegradable lubricants. The rules to predict how pour point of vegetable oil changes with dilution need to be established experimentally.

3.2 Composition and Effect of Pour Point Depressants (PPD)

There is a range of pour point depressant additives of different chemical species:

(i) Polymethacrylates

These are the most widely used pour point depressants, R in the ester (Figure 3.1) has a major effect on the product, and is usually represented by a normal paraffinic chain of at least 12 carbon atoms. This ensures solubility. The molecular weight of the polymer is also very important. Typically these materials are between 7000 to 10000 number average molecular weight. Commercial materials normally contain mixed alkyl chains which can be branched.

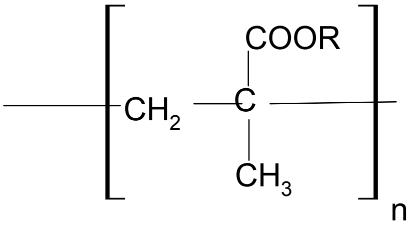


Figure 3.1: Polymethacrylate molecule

(ii) Polyacrylates

Polyacrylates are very similar in behaviour to the polymethacrylates. Figure 3.2 shows a polyacrylate molecule.

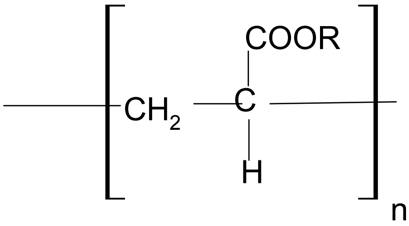


Figure 3.2: Polyacrylate molecule

(iii) Alkalated naphthalene

Alkalated naphthalene is condensation product of chlorinated paraffin wax with naphthalene (Figure 3.3).

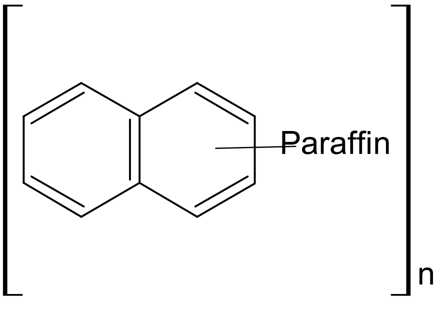


Figure 3.3: Alkalated naphthalene molecule

Most of the commercially available pour point depressants are polymethacrylate based (Asadauskas and Erhan, 1999) or alkylated polystyrenes (Aboul-Gheit, *et al.*, 1997). Pour point depressants act through surface adsorption on the wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. In the absence of long interlocking crystals or swollen particles, oil can move freely through any solid wax particles that are present. The limitations of pour point depressants are controlled by the nature of the lubricating oil and the concentration of the pour point depressant. The effect of pour point depressant varies widely with respect to the oil but they are most effective with thinner oils such as SAE 10, SAE 20, and SAE 30 grades. With SAE 50 grade oil only small effects are seen. Different types of pour point depressant also have different efficiencies, with maximum effect occurring at an optimum concentration level. Above this optimum level there is usually a visible effect on viscosity at higher temperatures. Typical levels of application of commercial oils are 0.1 to 1.0% (Crawford *et al*., 1997).

Paraffin wax deposition from middle distillate fuels at low temperature is one of the serious and long-standing problems in petroleum industry. At low temperatures, the crystals of wax easily form impermeable cakes, which can block filters and eventually lead to engine failure. Many methods have been attempted for the prevention of crystals mating together such as the application of chemical additives like pour point depressants (PPDs), cold flow improvers, paraffin inhibitors, wax crystal modifiers etc. It has been found that, with the addition of the additives, the shape of the wax crystal changes. Many postulates have been put forward to explain this phenomenon and to guide the PPD product design. Among the mechanisms adsorption co-crystallization, nucleation and improved wax solubility are widely accepted by mechanism researchers like Coutinalo *et al*. (2000), El-Gamal *et al*. (1998), Zhang *et al*. (2004), and El-Gamal and Al-Sabagh (1996). The wax deposition inhibitors are polymeric compounds that constitute a hydrocarbon chain and a polar segment. Hydrocarbon chain provides interaction between the additive and paraffin. The polar segment is responsible for wax crystal morphology modification, inhibiting the aggregation stage. For this reason, such inhibitors are known as wax crystal modifiers (Purohit *et al*., 2003). Several polymers which can be used as PPDs and/or flow improvers for middle distillate fuels vary greatly and belong to different chemical groups, such as long alkyl chain fatty acid.

3.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will flow into it than the reference to keep both at the same temperature. Whether more or less heat should flow to the sample depends on whether the process is endothermic or exothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of energy absorbed or released during such transitions (Smallman and Bishop, 1999).

A typical differential scanning calorimeter consists of two sealed pans: a sample pan and a reference pan (which is generally an empty sample pan) as shown in Figure 3.1. These pans are often covered by or composed of aluminum, which acts as a radiation shield. The sample is generally placed in an aluminum sample pan, which is then placed in the sample cell. The reference consists of a matched empty aluminum sample pan that is placed in the reference cell of the instrument. The sample pans are designed to have a very high thermal conductivity. Sample sizes generally range from 0.1 to 100 mg. The instrument cells are often airtight in order to shield the sample and reference from external thermal perturbations. This also allows experiments to be performed under variable pressures and atmospheres. The two pans are heated or cooled uniformly while the heat flow difference between the two is monitored. This can be done at a constant temperature (isothermally), but is more commonly done by changing the temperature at a constant rate, a mode of operation that is also called temperature scanning.

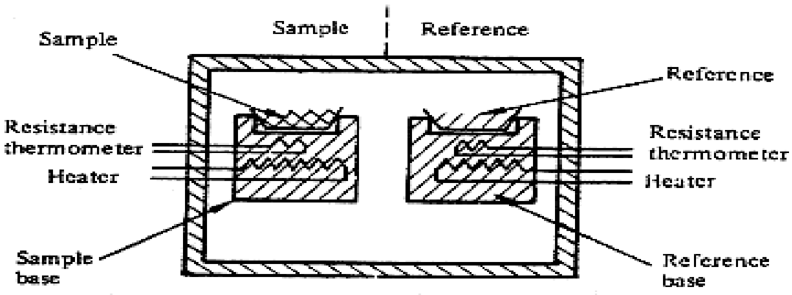


Figure 3.4: DSC experimental arrangement

During the experiment, the instrument detects differences in the heat flow between the sample and reference. This information is sent to an output device, most often a computer, and results in a plot of the differential heat flow between the reference and sample cell as a function of temperature. When there are no thermodynamic chemical processes occurring, the heat flow difference between the sample and reference varies only slightly with temperature, and shows up as a flat or very shallow base line on the plot. However, an exothermic or endothermic process within the sample results in a significant deviation in the difference between the two heat flows. The result is a peak in the DSC curve.

3.4 Experimental Details

3.4.1 Determination of Pour Point by ASTM D97 Method

The pour point of oil is the temperature below which the oil ceases to flow when it is cooled. In order to determine the pour point, the oil is first heated to 45°C in a water bath maintained at 48°C. It is then cooled at a specific rate (by maintaining the specified temperature of the cooling media) and at decrements of 3°C, the container is tilted to check for any movement. The temperature 3°C above the point at which the oil stops moving is recorded as the pour point. As per ASTM D97 method, pour point of mineral oils is defined as the lowest temperature at which movement of the test specimen is observed under the prescribed conditions of the test. In the case of vegetable oils, if the sample is kept under the same condition for an additional period of time, they re-melt and again solidify at a higher temperature. Hence the temperatures of the samples, after 15 minutes of recording the pour point temperatures as described above, are also recorded. As per ASTM D97 method pour points are measured in steps of 3 ºC, whereas the solidification temperatures on holding for 15 minutes are recorded in steps of 1 ºC.

The vegetable oils tested as described above were castor oil, coconut oil, groundnut oil, linseed oil, mustard oil, olive oil, palm oil, and sunflower oil. Refined and bottled oils purchased from the local market were used for the test.

3.4.2Analysis of Pour Point by Differential Scanning Calorimetry

DSC experiments were done on DSC-model Mettler Toledo DSC 822e, USA with a computer-based controller. This model has a temperature accuracy of ± 0.2 ºC, temperature measurement range of -150 ºC to 700 ºC and a measurement resolution of 0.04 mW at room temperature. Before each experiment, the DSC cell was purged with low-pressure nitrogen gas. Typically 10 mg of the oil sample was accurately weighed in an open aluminium pan and placed in the DSC module with a similar empty pan as reference.

The following DSC experiments were conducted on the oil samples listed in the last section;

a) Cooling experiments

b) Heating experiments

c) Isothermal experiments

In the cooling experiments, the sample was initially heated to 50°C and then held under isothermal condition for 10 minutes. This helps in dissolving and homogenizing any waxy material present in the oil, which may inadvertently act as seed to accelerate wax crystal formation during cooling. The system was then cooled to -50°C at a steady rate of 10°C/ minute using liquid nitrogen as the cooling medium. The cooling experiments were conducted at 0.1 °C/ minute, 0.5°C/minute, 1 °C/minute[1], 5°C/minute, and 10 °C/minute. In the heating experiments, the oil samples were initially cooled to -50°C using liquid nitrogen. The samples were then heated at a programmed rate of 1 °C/minute, 5 °C/minute, and 10 °C /minute until the temperature reaches 50°C. Isothermal experiments were conducted on coconut oil at 15 °C/minute, 18°C/minute, 21°C/minute and 24 °C/minute. In all experiments nitrogen was used as the purge gas. DSC experiments were performed on different vegetable oils listed in Table 2.2. Average value of three independent measurements was taken in each case.

3.4.3 Experiments with coconut oil added with PPD

A commercial polymethacrylate based PPD (obtained from Lubrizol, Chennai, India) was added in different percentages (by weight) from 0.1 to 0.5 to coconut oil and the pour points were determined in each case. Coconut oil was selected for the study as it has very high pour point because of the predominantly saturated fatty acid composition. Styrenated phenol (SP) is added in different concentrations from 1 to 20% and the pour point is determined in all cases by ASTM D97 method. DSC analysis was also performed in each case. SP was tried as an additive as it has shown to be a good anti-oxidant with coconut oil (Jayadas, 2007).

3.5 Results and Discussion

3.5.1 Analysis of cold flow properties of vegetable oils

Pour point (PP) is the most important low temperature property of any oil used as a lubricant. Pour points of vegetable oils tested are tabulated in Table 3.1. The temperatures (PP*) at which the oil congeals on holding for 15 minutes after recording the pour point values as per ASDTM D97 method are also tabulated in Table 3.1. Since the pour point temperatures are noted in steps of 3 ºC, the actual values may be still lower. For example, the temperatures at which coconut oil still flows (test for fluidity as per ASTM D97 method) may be 19, 20 or 21 ºC but the pour point will be recorded as 21 ºC. The congelation temperature (PP*) recorded after 15 min are higher than the pour points (PP) for all the vegetable oils tested. This observation is consistent with the findings of Adhvaryu *et al.* (2005), Rhee *et al.* (1995) and Kassfeldt and Goran (1997) that most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification much above the pour point upon long term cold storage. Kinker (2000) evaluated the cooling rate in ASTM D97 method as approximately 0.6 ºC/minute. At cooling rates above 0.1 ºC/minute vegetable oils tends to solidify in to low melting 'α' crystalline form (Cebula and Smith; 1991).

Table 3.1: Pour points of vegetable oils by ASTM D97 method

Sl. No	Oil	Pour point(°C) ASTM D97	Temperature(°C) after holding for 15 min (PP*)	Remarks
1	Castor oil (A)	-33	-27	-
2	Coconut oil (B)	21	24	-
4	Groundnut oil (D)	3	5	-
4	Linseed oil (E)	-30	-27	-
5	Mustard oil (F)	-18	-15	-
6	Olive oil (G)	-9	-5	-
7	Palm oil (H)	*	5	*Poor repeatability
8	Sunflower oil (I)	-18	-16	-

DSC thermograms (at 10 ºC/minute in both cooling and heating) for three typical vegetable oils i.e. sunflower oil (poly- unsaturated), olive oil (mono-unsaturated) and coconut oil in cooling and heating are shown in Figure 3.5 and 3.6.

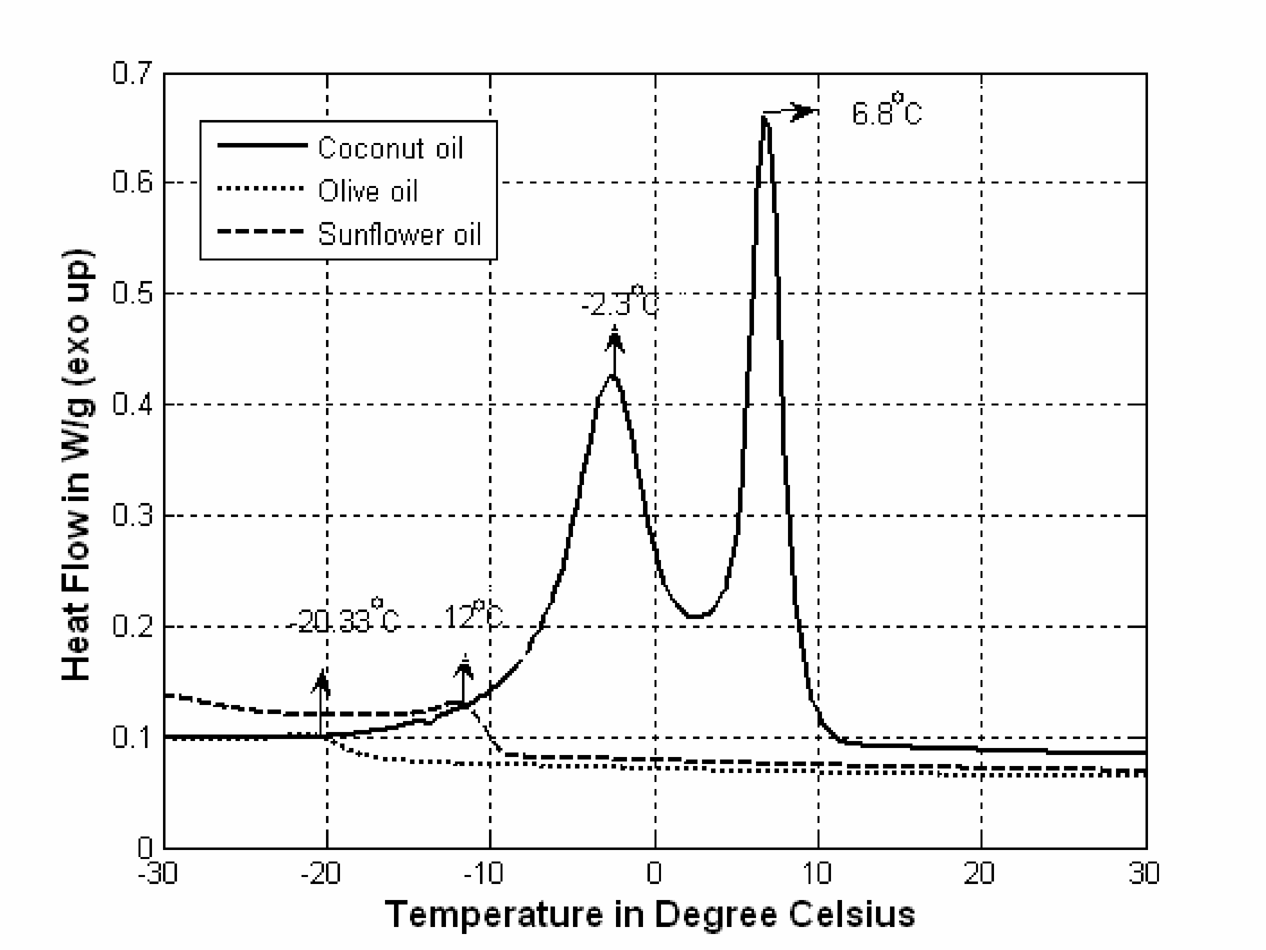


Figure **3.5: DSC Thermogram of coconut oil, olive oil and sunflower oil in cooling**

The peak values in the cooling curves are considerably lower than the peak values in heating. The peak values in heating thermograms are closer to the congelation temperature PP*. Previous studies have shown that in cooling experiments, cooling rates and thermal history can influence the shape of the thermograms as well as the corresponding temperatures obtained (Jiang *et al.*, 2001). Aboul-Gheit *et al.* reports the effectiveness of DSC traces obtained in heating experiments (endotherms) in analyzing the effect of additives in the melting behaviour of base oils. Because wax recrystallizes into high melting stable polymorph before melting, DSC traces in melting do not show much variation in the onset, peak, and end temperatures of endothermic heat flow.

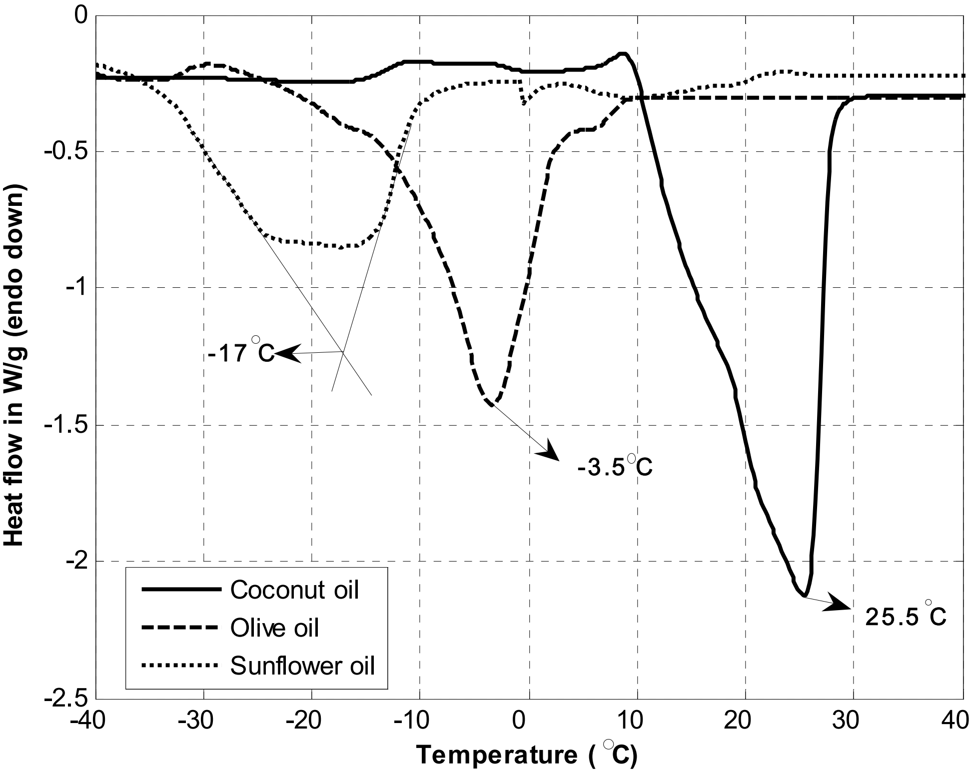


Figure **3.6: DSC Thermogram of coconut oil, olive oil and sunflower oil in heating**

Since the heating and cooling thermograms of coconut oil shows pronounced difference, results of further DSC analysis are discussed. Figures 3.7 and 3.8 show DSC thermograms of coconut oil in cooling and in heating. DSC thermogram in cooling shows two peaks at lower temperatures than the single peak in heating thermogram. In heating thermogram two exothermic peaks one between -15 ºC and 0 ºC and another between 0 ºC and 10 ºC are visible. These peaks correspond to the peaks between -18 ºC and 2.8ºC and 2.8 ºC and 12 ºC in the cooling experiments. These observations are consistent with the findings of Cebula and Smith (1991) that at high cooling rates vegetable oils crystallize in to low-melting polymorphs α and β'. In heating vegetable oil re-crystallizes in to β' and β before melting.

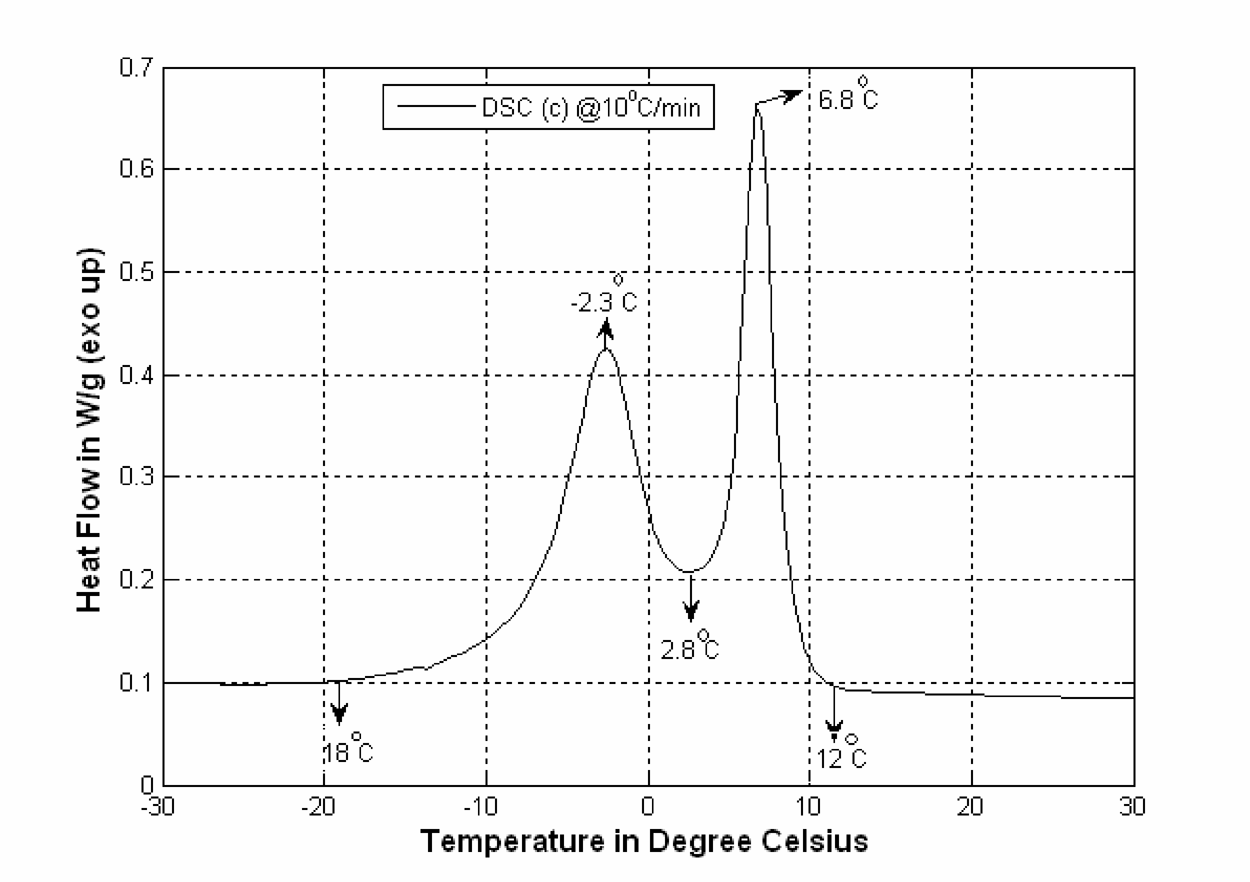


Figure 3.7: DSC thermogram of coconut oil in cooling @10 °C/minute

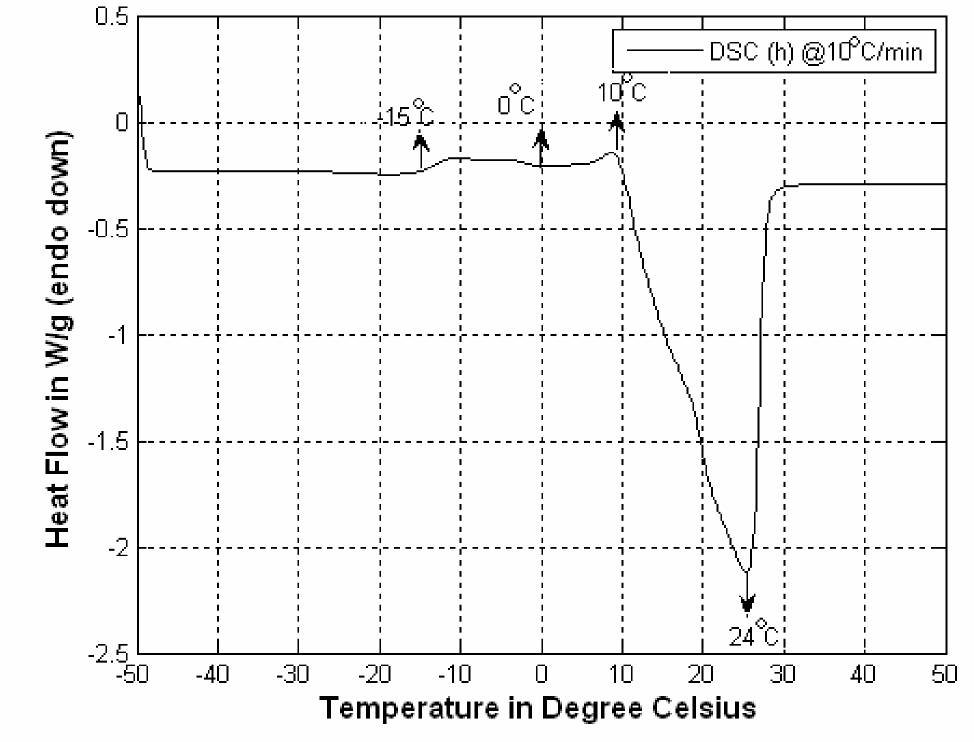


Figure 3.8: DSC thermogram of coconut oil in heating @10 °C/minute

Figure 3.9 shows DSC thermograms of coconut oil at different cooling rates (0.1, 0.5 and 1ºC/minute). As the cooling rate decreases coconut oil crystallizes in to only one crystalline form. At the cooling rate of 0.1ºC/minute the peak temperature increases to 23ºC which is near to the congelation temperature. The heating rate influences the size of the thermogram, but do not significantly alter the onset, peak, and end temperatures (Figure 3.10). This result is in consistence with the earlier observation that the onset, peak, and end temperatures of endothermic heat flow in heating experiments do not show much variation (Cebula and Smith; 1991).

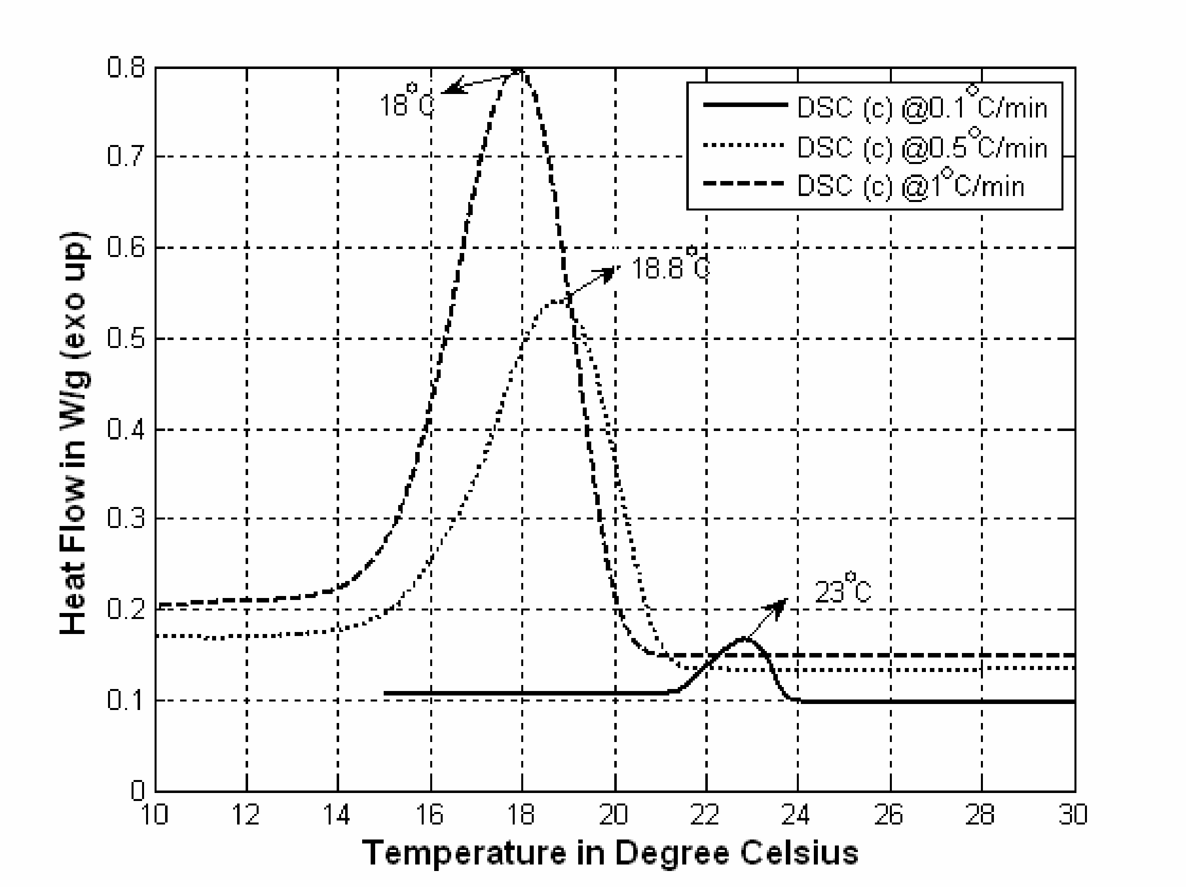


Figure 3.9: DSC thermograms of coconut oil at different cooling rates

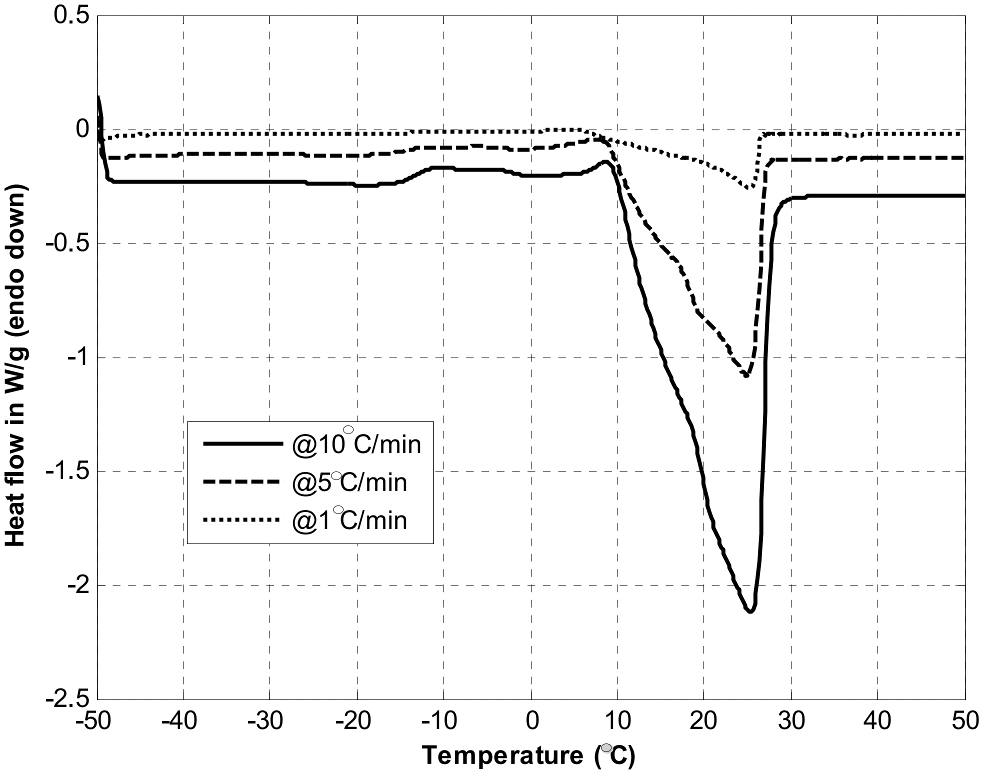


Figure 3.10: DSC thermograms of coconut oil at different heating rates

Since melting is an endothermic reaction, heat flow (to the sample) increases as melting starts. Being mixed triglycerides having different fatty acid constituents vegetable oils melt over a range of temperatures. Coconut oil contains more than 90% saturated fatty acids (lauric, myristic and palmitic). In olive oil, nearly 80% of fatty acid content is oleic acid. Sunflower oil contains both oleic and linoleic acid which has different packing characteristics in crystallization. Coconut oil and olive oil show broad endothermic traces with unique peaks at 25.5 ºC and -3.5ºC respectively (Figure 3.5). On the other hand, DSC trace of sunflower has two blunt peaks near -17 ºC. The peaks in sunflower oil correspond to oleic acid (with higher melting point) and linoleic acid. Sesame oil also has similar DSC trace with two blunt peaks (not shown). Sunflower oil and sesame oil contain oleic acid and linoleic acid in almost equal proportions. Palm oil contains both saturated fatty acid (palmitic acid) and mono-unsaturated fatty acid (oleic acid) in nearly equal amount. The DSC thermogram (Figure 3.11) of palm oil shows different peaks corresponding to different fatty acid constituents. The temperatures at endothermic peak of all the oils tested are tabulated in Table 3.2. Castor oil and linseed oil show very low endothermic peak temperatures. This can be attributed to the nature of their fatty constituents namely ricinoleic acid (with a hydroxy group) and linolenic acid (3 double bonds) respectively. Groundnut oil contains both saturated and unsaturated fatty acids and hence shows multiple peaks. Though the major endothermic peak is at -14.5ºC (Figure 3.12), due to the influence of the unsaturated fatty acid content, congelation takes place at 3ºC. The temperature values are average of three independent experiments performed on the same sample at a heating rate of 10 ºC/ minute.

Table 3.2: DSC endothermic peaks in heating experiments for different oils

Sl No	Oil	Endothermic peak (°C) and repeatability	Remarks
1	Castor oil (A)	-26.2±2.2	-
2	Coconut oil (B)	25.3±0.7	-
3	Groundnut oil (C)	-	Multiple peaks
4	Linseed oil (D)	-14.5±0.9	-
5	Mustard oil (E)	-28.9(±0.4)	-
6	Olive oil (F)	-15.3±(1.5)	-
7	Palm oil (G)	-3.8±0..6	Multiple peaks
8	Sunflower oil (H)	-17.2±1.3	-

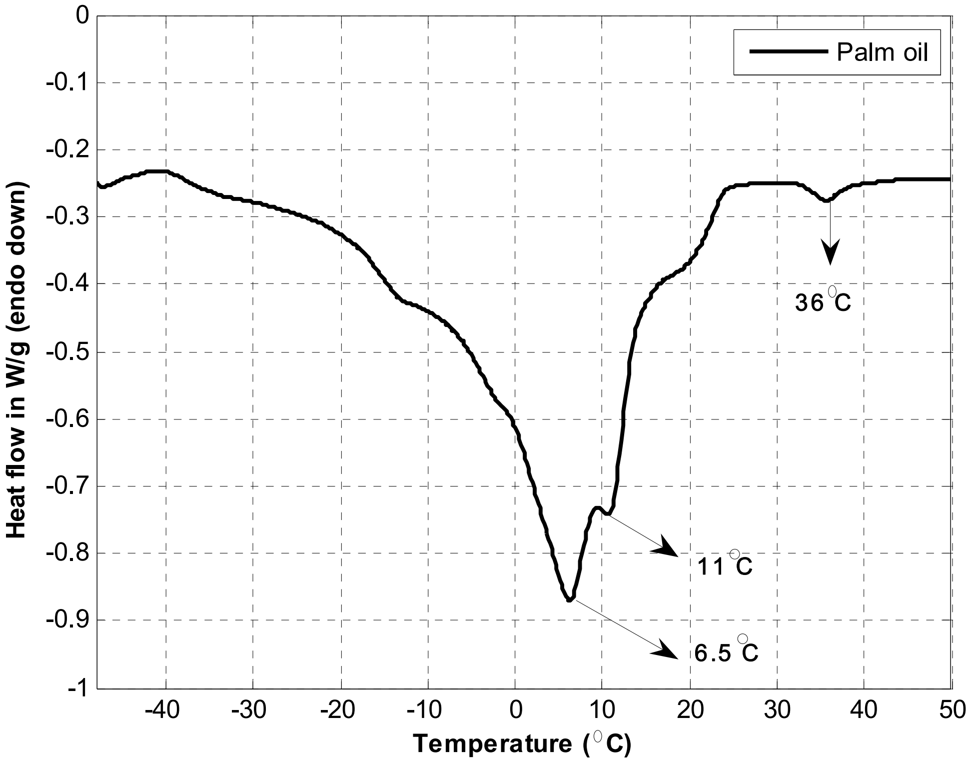


Figure 3.11: DSC thermogram of palm oil

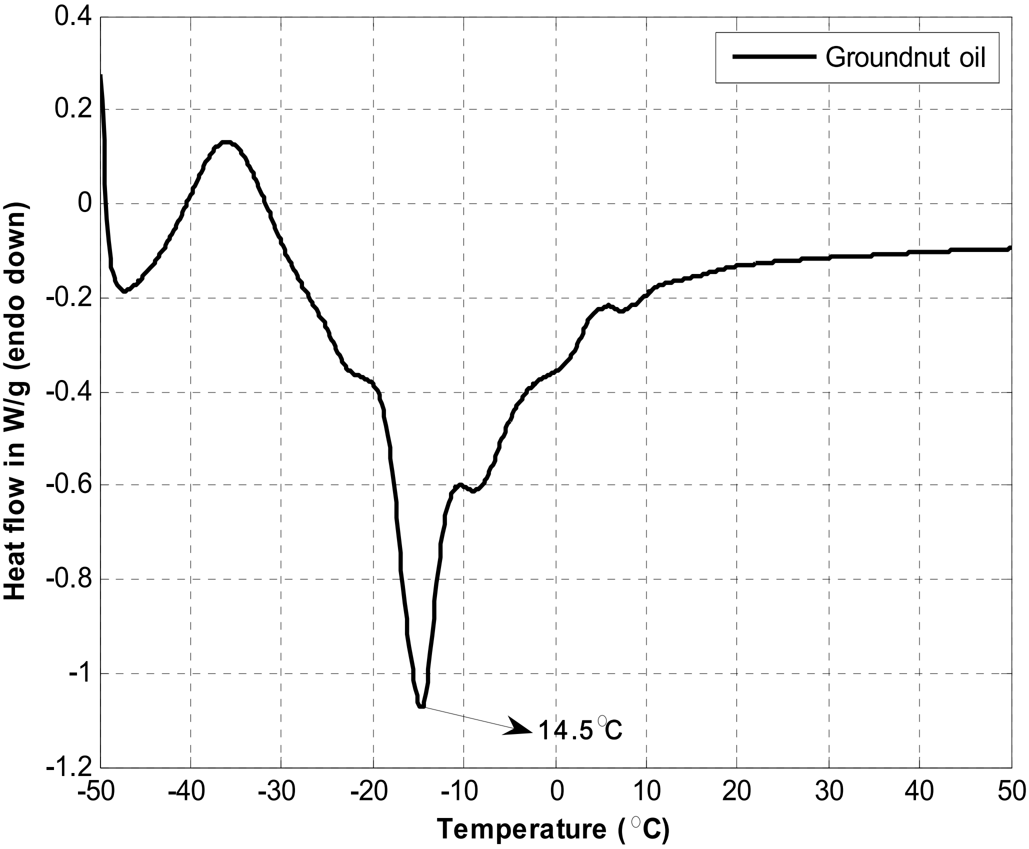


Figure 3.12: DSC thermogram of groundnut oil

3.5.2 Analysis of the effect of additives on cold flow properties

Pour point depressants (PPD) have been created to suppress formation of large crystals during solidification, although the mechanism of PPD action on triacylglycerol crystallization remains undisclosed (Asadauskas and Erhan, 1999). Typically, commercial PPD are known to contain a polymethacrylate backbone with a certain type of branching, which allows inclusion of the PPD molecule into the growing crystal. Table 3.3 shows the effect of different quantities of a polymethacrylate based PPD on the pour point of coconut oil. These results conclusively prove the ineffectiveness of the commercial PPD used, in bringing down the pour point of coconut oil in a significant manner. The DSC thermograms also did not show any significant difference with different concentrations of the PPD.

Table 3.3: Pour point (by ASTM D97 method) of coconut oil with poly methacrylate based commercial PPD

PPD (%)	0.1	0.2	0.3	0.4	0.5
Pour Point (ºC)	24	21	18	18	18

The effect of the addition of styrenated phenol (SP) is shown in Table 3.4. DSC Thermograms (heating) of coconut oil with SP in different concentrations are shown in Figure 3.13. The peaks corresponding to re-crystallization before melting (two peaks) and melting is seen shifted to the low temperature region with a subsequent reduction in pour point (Table 3.4). The effect of SP tapers off at 15% and further addition does not bring down the pour point.

Table 3.4: Pour point of coconut oil additive (styrenated phenol) mixture

Coconut oil + Additive (BA)	**Pour point (ºC) (ASTM D97)**
0% SP	24
1% SP	24
2%SP	24
3%SP	21
4%SP	21
5% SP	15
10% SP	15
15% SP	12
20% SP	12

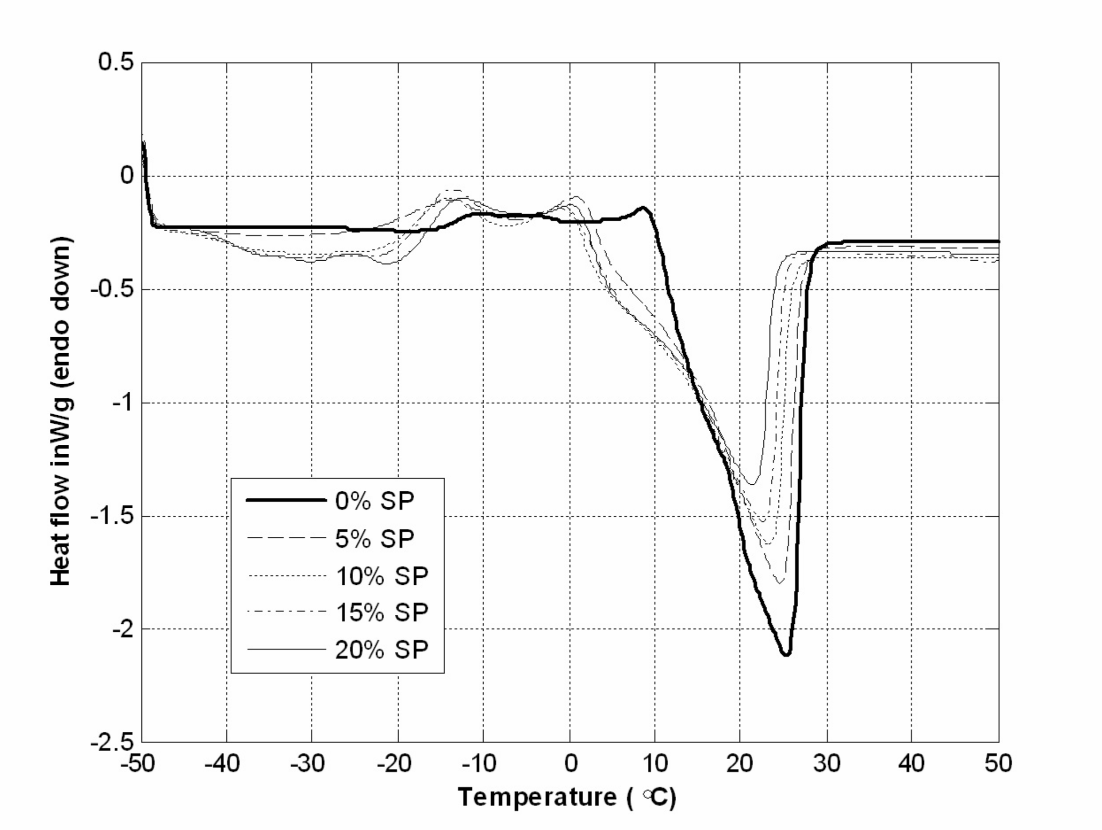


Figure 3.13: DSC Thermograms (heating) of cocout oil with styrenated phenol (SP)

3.6 Conclusions

Vegetable oils solidify at higher temperatures than the pour points determined by the ASTM D97 method on prolonged storage at low temperature. At the cooling rate as employed in ASTM method vegetable oils crystallize in to low melting α polymorph which on prolonged storage re-crystallizes in to higher melting polymorphs β and β'. DSC thermogram captures the thermal activities (melting, crystallization etc.) in vegetable oils as they are heated or cooled at different rates. Cooling thermograms are rate dependent whereas heating thermograms are independent of heating rate as far as position of peaks (crystallization or melting) are concerned. Hence, DSC (heating) is proven to be an ideal tool for analyzing the low temperature properties of vegetable oils.

Addition of SP caused significant reduction of pour point from 24 °C to 12°C when 15% SP was added. But increasing addition of SP more than 15% was found to be ineffective in reducing pour point below12°C. The pour point obtained (12°C) is still much higher than that is required for any lubricant application (-6°C for two-stroke engine lubricant as per IS14234).

Chapter 4

Interesterification

4.1 Introduction

Efforts have been made to improve the low-temperature properties by blending the vegetable oils with diluents such as poly α olefin, diisodecyl adipate, and oleates (Asadauskas and Erhan, 1999). The effect of diluents and pour point depressants (PPD) on vegetable oils has been unsatisfactory. The other possible way to control these obstacles is structural modification of the oils by chemical reaction (Erhan and Asadauskas, 2000). It has been reported that triacylglycerols with more diverse distribution of fatty acids on the glycerol backbone have lower solidification temperatures (D'Souza *et al.*, 1991). Chemical modification of the vegetable oils to give more complex structures should improve the low-temperature properties (Wagner *et al.*, 2001).

Interesterification (IE) is the process of re-arranging the fatty esters within and between triglycerides resulting in most cases, a change in the physical properties of the oil/fat. It is a useful modification method to give the oil/fat the functionality required for a finished product. Erhan and Asadauskas (2000) reported that modification (interesterification) route can be applied to improve the pour point of vegetable oils. Interesterification is the intra and intermolecular exchange of fatty acids on the glycerol backbone of triacyglycerols, although the term is used loosely to include acidolysis and other ester exchange reactions. It is applied to either an individual oil or blend of oils, to produce triacylglycerol with different properties. The molecular species of natural triacylglcerols is not a random mixture of all possible isomers, but it shows greater or lesser selectively in the distribution of fatty acids (Gunstone, 1999). This as well as the overall fatty acid "*cis*" mixture, determines many of the technically important properties of the oil or fat, for example, solid fat content and the melting point. Once subjected to interesterification with a chemical catalyst, the triacyglycerol become a random mixture of molecular species (Scrimgeour, 2005). Figure 4.1 shows a general interesterification reaction.

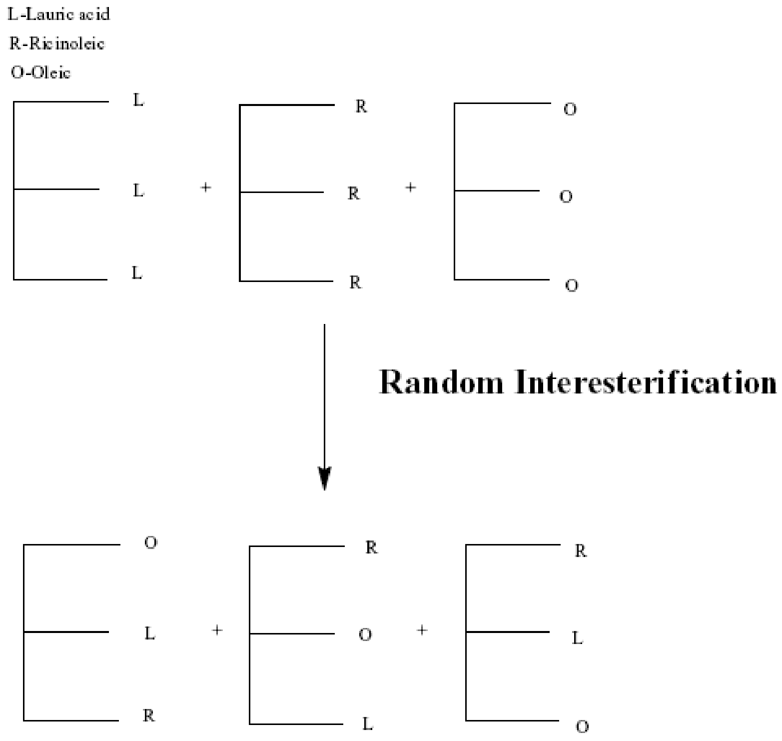


Figure 4.1: Random intersterification reaction

The random or chemical IE is the most applied IE modification process of oils and fats as it is simpler, cheaper and easier to carry out compared to directed or enzymatic IE. Chemical IE can be carried out by applying the following conditions:

- heat at > 300°C;
- heat with caustic soda at 200°C;
- heat with sodium methoxide or ethoxide at 80°C-100°C;
- heat with metallic sodium at 100°C-120°C; and
- heat with sodium/potassium alloy at 0°C.

Although IE can occur without a catalyst, the process requires a long time and high temperatures such as 300°C, which can cause the formation of undesirable by-products. On the other hand, the catalyst speeds up the reaction and lowers the temperature of reaction. Only the third and fourth of the processing conditions are widely used today. The commonly used catalysts are sodium methylate and ethylate followed by sodium metal, Na/K alloy and the hydroxides of Na and K in combination with glycerol. Some of these catalysts are shown in Table 4.1. Sodium methylate and ethylate can be used as a dry powder or liquid *i.e.*, dispersed in a solvent such as xylene. They are inexpensive, easy to handle, react at low temperatures of 50°C-70°C, used in very low rates (0.1% if the starting material is well refined and dried; 0.2%-0.4% on average) and easily removed by simple water washing after the reaction. However, the drawbacks are their widely varied quality, the need for an induction period before the reaction starts and the loss of oil due to formation of soap and methyl esters upon removal of the catalyst by washing with water (Sreenivasan, 1976). Though the loss of oil can be minimized by introducing carbon dioxide along with water during deactivation of the catalyst, the system will only work efficiently if there is a time lag between the catalyst neutralization and centrifuge separation of the fat and water phases (Going, 1967).

Table 4.1: Interestrification catalysis

Type	Example	Required Dosage (% Oil Weight)	Time
High Temperature (120 ºC-260 ºC)			
Metal Salts	Acetates,Carbonates,Chlorides,Oxides of Zn,Fe ,etc	0.1%-0.2%	0.5-6 Hours under vacuum
Alkali Hydroxides	NaOH,KOH,LiOH,or Sodium Hydroxide+Glycerol	0.2%	45 minutes-1.5 Hour under vaccum
Metal Soaps	Sodium Stearate +Glycerol	0.5%-1%	1Hour under Vacuum
Low Temperature (25 ºC-270 ºC)			
Metal Alkylates	Sodium Methylate	0.1%-1.0%	5-120 Minutes
Alkali Metals	Na,K,Na/K Alloy	0.2%-0.5%	3-120 Minutes
Alkali Metal Hydrides	Sodium Hydride	0.2%-0.5%	30-120 Minutes
Alkali Metal Amides	Sodium Amide	0.15%-0.2%	10-60 Minutes

Coconut oil has very high saturated fatty acid content (Table 2.2) and has a correspondingly high pour point (Table 3.1). Since the unsaturated fatty acid content of coconut oil is less than 10% random interesterification among the coconut oil is unlikely to have a noticeable influence in the pour point of coconut oil. Castor oil and sunflower oil have very low pour points compared to coconut oil (see Chapter 3 Section 3.4.1). Keranja oil (pongammia pinnatta) is atropical non-edible oil which also has a low pour point compared to coconut oil. The major fatty acid constituent of castor oil is recinoleic acid (12-hydroxy-9-cis-octadecenoic acid) and that of sunflower oil are oleic acid (9-cis-octadecenoic acid) and linoleic acid (9-cis, 12-cis-octadecadienoic acid). Keranja oil also has high oleic acid and linoleic acid content. Mixtures of these oils with coconut oil will have diverse fatty acid content, which on random interesterification can lead to re-distribution of fatty acids among triacylglycerol molecules producing better pour point for the mixture.

4.2 Experimental Details

The interesterification process was conducted in the following manner. Edible grade, refined, and commercially available coconut oil 100 g was taken in a round bottomed flask. Coconut oil is then mixed with different vegetable oils like castor oil, sunflower oil, Keranja oil in different proportions (by % weight). The flask with the mixture was placed on a heater with magnetic stirring attachment. A magnet was dipped in the oil mixture for stirring purpose. The mixture was heated at a constant temperature of 180^{o}C, for 1 hour with continuous stirring. After 1 hour, any moisture content in the flask was removed by vacuum pump. Sodium metal (Na) was added to the mixture as catalyst. Amount of sodium was 2 g (1% by weight). Heating and stirring was continued again up to 3 hours. Then the mixture was cooled to room temperature and filtered. All the reaction was done at atmospheric pressure.

The vegetable oils used were commercially available refined oils purchased from local market. Sodium metal was laboratory grade.

4.3 Results and Discussion

Interesterification was carried out with different vegetable oil mixtures with coconut oil as one constituent and different other vegetable oils. Coconut oil castor oil mixtures (with concentrations varying from 90%, 80%, 70%, 60% and 50% coconut oil and corresponding concentrations of castor oil) did not show any difference in pour point before and after interesterification reaction. Sunflower oil and Keranja oil showed reduction in pour point in all concentrations. The maximum reduction in pour point occurred in mixtures containing 50% coconut oil. The values of pour point before and after interesterification reaction with 50% coconut oil are shown in the Table 4.2.

Table 4.2: **Values of pour point before and after Interesterification reaction**

Oil Mixture	Pour Point (By ASTM-D97 Method) in ºC	
	Before Interestrification	After Interestrification
Coconut (50%) + Castor (50%)	21	21
Coconut (50%) + Sunflower (50%)	21	18
Coconut (50%) + Keranja(50%)	21	18
Coconut (50%) + Sunflower (25%) + Keranja(25%)	21	18

DSC thermograms (heating) of coconut oil and sunflower oil are shown in Figure 3.6(Chapter 3). DSC thermogram (heating) of castor oil is shown in Figure 4.2. Figure 4.3 and 4.4 show DSC thermograms (heating) of coconut oil and castor oil and coconut oil and sunflower oil mixtures before and after interesterification. Figure 4.3 shows that interesterification does not produce any significant change in the heating thermogram for coconut oil castor oil mixture. In the case of coconut oil and sunflower oil mixture (Figure 4.4) interesterification results in evening out of peak corresponding to sunflower oil (see Figure 3.6, chapter 3). The pour point value as shown in Table 4.2 reflects this change, though not very significant. Coconut oil- keranja oil and coconut oil-keranja oil-sunflower oil mixtures also show slight decrease (3 ºC) in pour point temperatures (Table 4.2). The ineffectiveness of interesterification of coconut oil with castor oil can be attributed to the consumption of catalysts (sodium in the present case) by the saponification of hydroxyl group of resinoleic acid (12-hydroxy-9-cis-octadecenoic acid). .

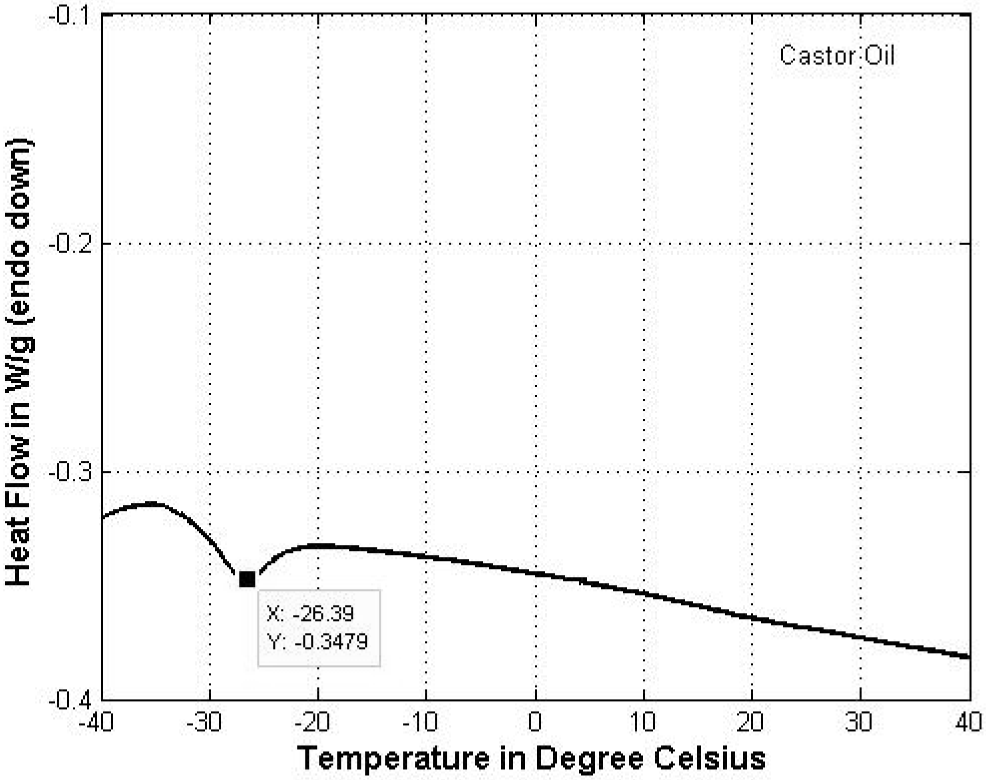


Figure 4.2: DSC Thermogram (heating) of castor oil

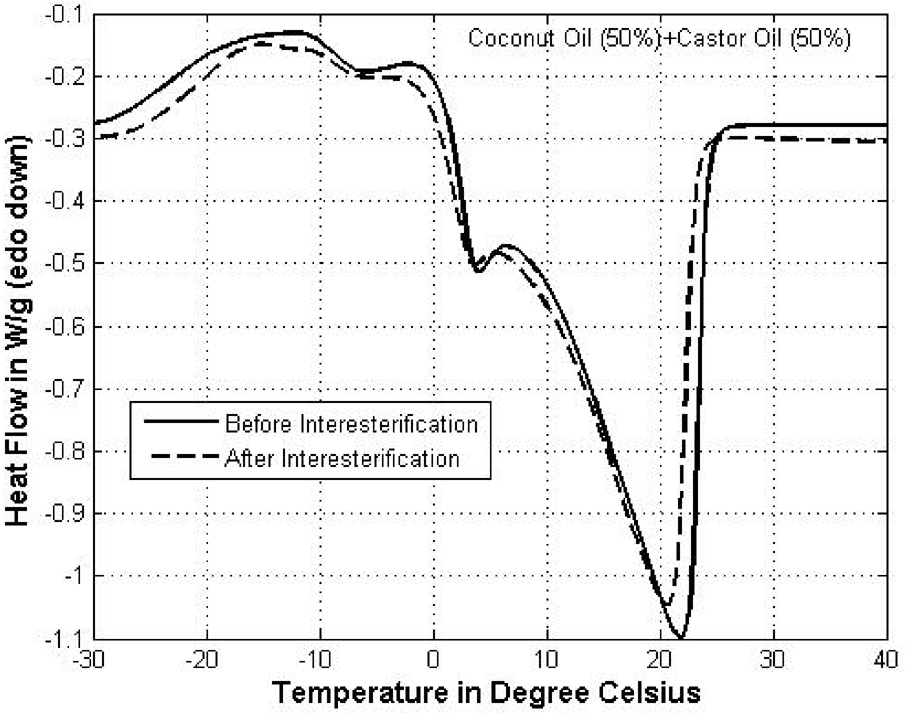


Figure 4.3: DSC thermogram (heating) of coconut oil, castor oil mixture

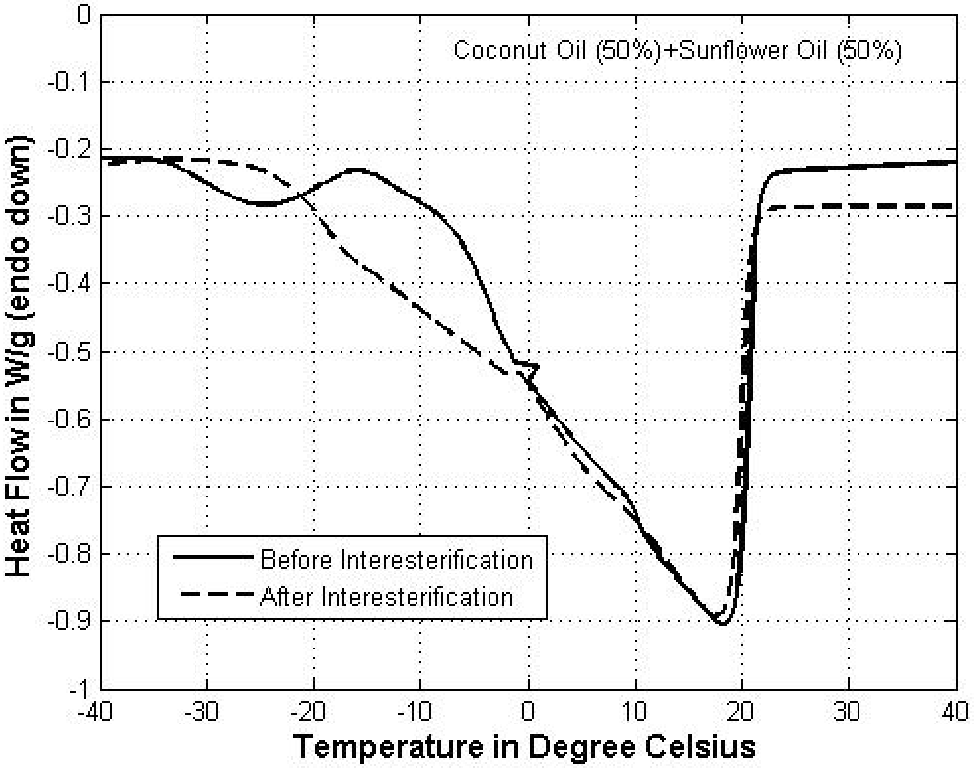


Figure 4.4: DSC thermogram (heating) of coconut oil,sunflower oil mixture

4.4 Conclusions

Coconut oil due to the predominantly saturated nature of its fatty acids has very high pour points. Interesterification of Coconut Oil with other vegetable oils was found to be not very effective in lowering the pour point of coconut oil. DSC analysis has shown that there is always a peak corresponding to the solidification of the triacylglycerol molecules with predominantly saturated fatty acid content (lauric acid). The wax formation at high temperature may lead to other low melting components leading to the formation of gel like structure. While interesterification of Coconut oil with Caster oil was found to be ineffective in reducing pour point, the process with other vegetable oils such as Sun flower oil and Keranja Oil yielded 2 to 3 ^{o}C reduction in pour point.

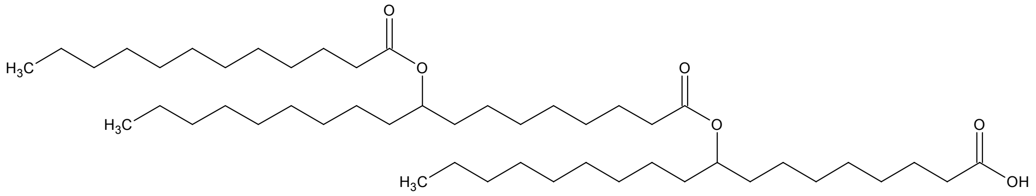
Chapter 5

Synthesis and Evaluation of Esterified Estolide

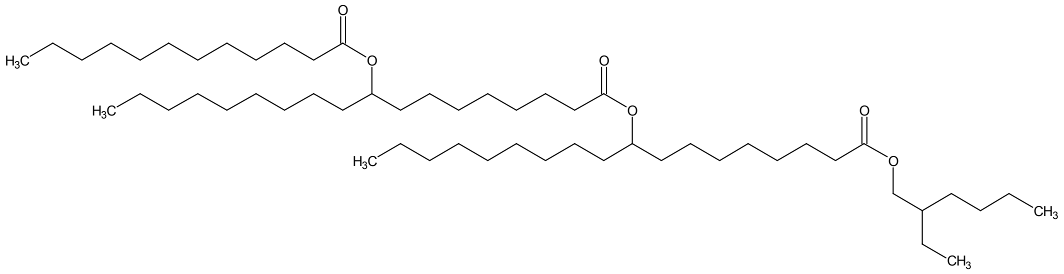
5.1 Introduction

Coconut oil has a very high congelation temperature precluding its use as base oil for industrial lubricants in temperate and cold climatic conditions. On the other hand vegetable oils with high degree of poly-unsaturation have comparatively better low temperature properties. Asadauskas and Erhan, 1999 reports exhaustive studies on the depression of pour points of vegetable oils by blending with various diluents and pour point depressants (PPD). They conclude that the diluents and PPDs provide only limited improvement in the low-temperature performance. In this work the initial attempts to reduce the pour point of coconut oil with commercial PPDs known to contain a polymethacrylate backbone showed unsatisfactory results (Chapter 3). Wagner *et al* (2001) reviews many chemical modification processes suitable for vegetable oils to improve their base oil properties including cold flow characteristics. Vegetable oils have a tendency to form macro crystalline structures at low temperature through uniform stacking of 'bend' triacylglycerol backbone (Adhvaryu *et al*., 2005). Attachment of side chains at double bond positions by chemical modification procedures like oligomerization (synthesis of dimers, estolides etc.) and alkoxylation is suggested as possible methods to improve cold flow behaviour of vegetable oils (Erhan and Asadauskas, 2000). Hence, in the present work chemical modification route to improve the pour point of coconut oil is attempted.

Estolides are fatty acid oligomers synthesized by the acylation at the double bond sites of unsaturated fatty acids. If an unsaturated fatty acid is used for acylation, acylation is again possible at the double bond site of the second fatty acid. In this manner oligomerization can be continued and it can be stopped with a saturated fatty acid. An estolide molecule from two oleic acid and a lauric acid molecules is shown in Figure 5.1. Isbell *et al*. (2001) and Cermak and Isbell (2003) describes the various synthetic procedures and properties of estolides and 2-ethylhexyl esters of estolides. Viscosity and other physicochemical properties are functions of the degree of oligomerization. In this work the synthetic procedure as described in Cermak and Isbell (2003) is adapted for the synthesis of 2-ethylhexyl ester of estolide; a) from coconut oil and castor oil, b) lauric acid (a major constituent of coconut oil) and oleic acid (a mono unsaturated oil). Since the double bonds get eliminated in the process the product is expected to have excellent oxidation stability. The branched structure is expected to impart improved cold flow properties. The cold flow properties and other important lubricant properties (viscometric, physicochemical, tribological, oxidative and corrosion) are evaluated subsequently and reported in the thesis.



Estolide with two oleic acid and one lauric acid molecules



2-Ethylhexyl estolide ester

Figure 5.1: A typical estolide and 2-ethylhexyl ester of estolide

5.2 Experimental Details

5.2.1 Modification of Cold-Flow Properties by Chemical Modification

Cermak and Isbell (2003) reported synthesis of 2-ethylhexyl esters of estolides (fatty acid oligomers) with excellent cold flow properties. The authors reported synthesis of lauric-oleic estolides that have great cold temperature properties. Cermak and Isbell (2003) used lauric acid and other medium chain fatty acids for the synthesis. Since coconut oil is a very rich source of medium carbon fatty acids, synthesis of estolides and subsequent esterification with 2-ethylhexanol was attempted in the present work. The acid catalyzed condensation reactions were conducted without solvent in a 500 ml, baffled, jacketed reactor with a three-neck reaction kettle cover. The reactor was connected to a recirculating constant temperature bath maintained at 60±0.1ºC. An overhead stirrer using Teflon coated shaft and a Teflon blade was used for mixing. The reactions were conducted at atmospheric pressure. The reaction was carried out with two reactant mixtures;

a) Reactant mixture containing coconut oil, castor oil and
b) Reactant mixture containing lauric acid and oleic acid.

Synthesis of estolide from vegetable oils (coconut oil and castor oil).

The acid catalyzed condensation reactions were conducted without solvent in a 500 ml, baffled, jacketed reactor with a three-neck reaction kettle cover. The reactor was connected to a recirculating constant temperature bath maintained at 60±0.1ºC. An overhead stirrer using a Teflon coated shaft and a Teflon blade was used for mixing. The reactions were conducted at atmospheric pressure. A reactant mixture containing 90g coconut oil, 10g castor oil, and 20.3g oleic acid was used. The reactant mixture was heated to 60ºC with overhead stirring. Once the desired temperature was reached, 3g (~0.4 eq., 1.8 mL) perchloric acid ($HClO_4$) was added drop wise to the mixture and the reaction vessel was stoppered. After 24 hour, 56.5g 2-ethylhexyl alcohol was added to the vessel and the mixture was stirred for 2 additional hours. The completed reactions were quenched by the addition of 2g potassium hydroxide (KOH) (1.2 equivalents based on $HClO_4$) in 90% ethanol water solution. The solution was allowed to cool for 30 minutes. The organic layer was extracted with hexane and dried over sodium sulphate and concentrated *in vacuo*.

Synthesis of estolide ester from vegetable oil fatty acids (lauric acid and oleic acid)

These reactions were also conducted without solvent in a 500 mL, baffled, jacketed reactor with a three-neck reaction kettle cover. Oleic acid (100g, 354mmol) and lauric acid (71g, 354 mmol) mixed together and heated to 60 ºC. All the reaction conditions were the same as for reactions carried out in the previous section. Once the desired temp was reached perchioric acid (0.05 equivalent, 35.4 mmol and 3.2 ml) was added. After adding perchloric acid, the reaction carried out for 24 hours. After 24 hours 2-ethylhexylalcohol (59.6g, 457.6mmol) was added to the vessel and the mixture was stirred for additional 2 hours. The completed reactions were quenched by the addition of KOH (35.6 mmol, 2g, 1.2 equivalent based on perchloric acid) in 90% ethanol water solution. The solution was allowed to cool for 30 minutes. The organic layer was extracted with hexane and dried over sodium sulphate and concentrated *in vacuo*.

Coconut oil used was commercially available edible grade oil. Oleic acid, lauric acid, castor oil, perchloric acid, 2-ethylhexyl alcohol, and potassium hydroxide were laboratory grade reagents obtained from Aldrich, a high grade laboratory chemical supplier.

5.2.2 FTIR Experiments

Infrared spectra were recorded on Thermo-Nicolet Avatar 370, FTIR spectrometer system. The regular scanning range used for the samples was 400-4000/cm. The signal to noise ratio was 3000:1, and a spectral resolution of 4/cm was used. The sample of chemically modified coconut oil was analysed in a standard cell having a fixed path length of 1mm. The spectra recorded were averaged over 32 scans.

5.2.3 NMR Experiments

^{1}HNMR and ^{13}CNMR data of the sample was recorded on JEOL GSX 400MHz machine at an observing frequency of 400.23MHz and 100.63MHz respectively. Deuterated chloroform ($CDCl_3$) was used to prepare the sample solution (15% w/v) containing 1% tetramethylsilane as an internal standard. The experiments were conducted at 23°C and 32 scans were taken for the sample.

5.3 Results and Discussion

Vegetable oils are mixed triglyceride esters of different fatty acids which can be saturated, unsaturated or poly-unsaturated (Adhvaryu *et al*., 2005). Many researchers, notably Adhvaryu *et al*. (2005), Wagner *et al.* (2001), Erhan and Asadauskas (2000), report that pour point of vegetable oils can be brought down by introducing branching in the fatty acid chains of vegetable oil molecules by suitable chemical modification processes. Such branching interferes with close packing of molecules during crystallization and hence brings down pour point. Double bond sites (bis-allylic, allylic and olefinic) in the mono- and poly-unsaturated fatty acids are the chemically favoured sites for introducing branching by appropriate chemical reaction. Since the unsaturated fatty acid content in coconut oil is comparatively low (approximately 7% of oleic acid and 2% of linoleic acid) it is desirable to mix it with some other oil with high degree of un-saturation like castor oil to make it amenable to chemical modification processes that can bring down pour point. Low temperature properties of coconut oil can also be modified by attaching long chain molecules at the double bond sites by suitably designed chemical processes.

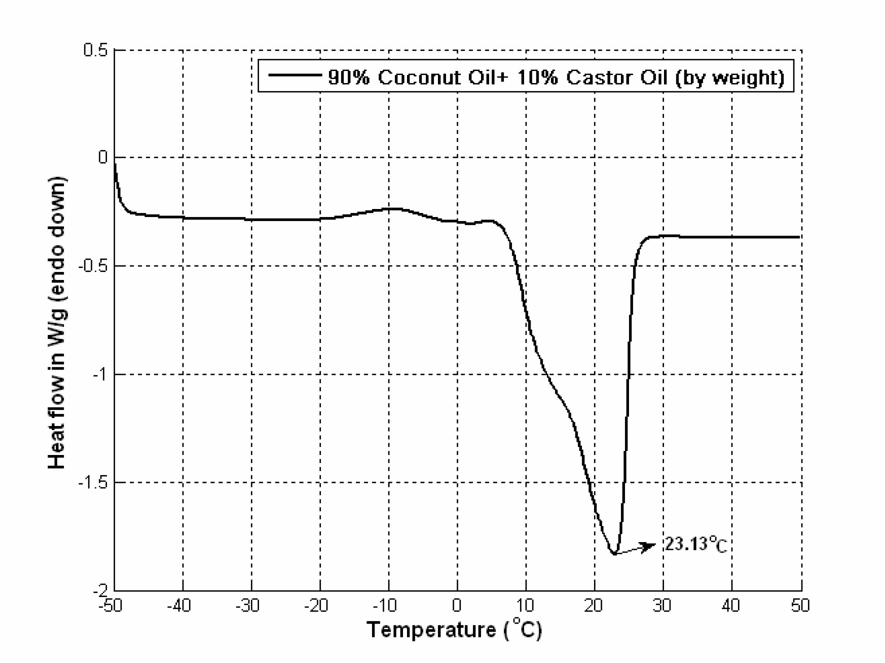


Figure 5.2: DSC Thermogram of 90% coconut oil+ 10% castor cil (by weight)

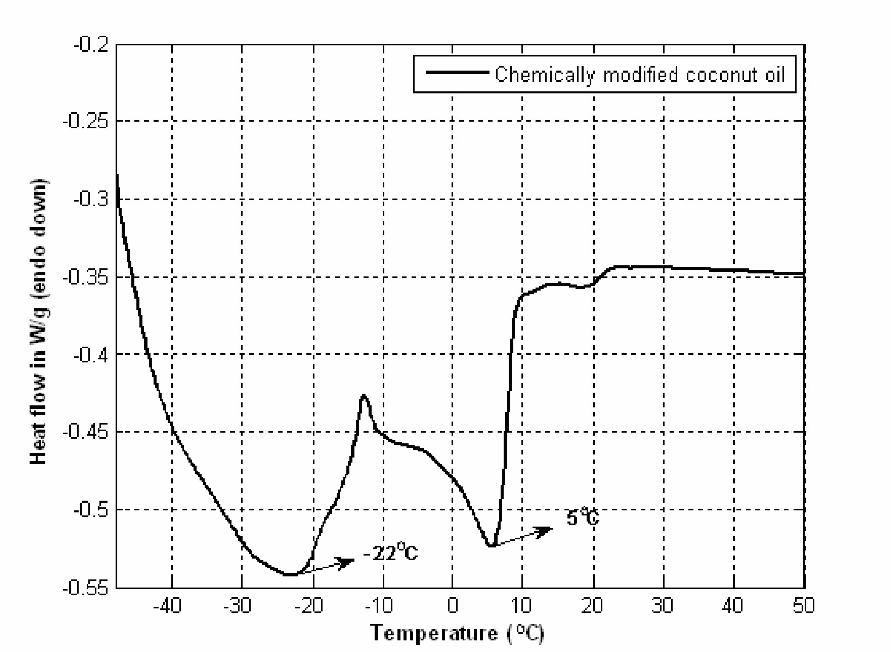


Figure 5.3: DSC Thermogram chemically modified coconut oil (from coconut oil and castor oil-Section 2.1.1)

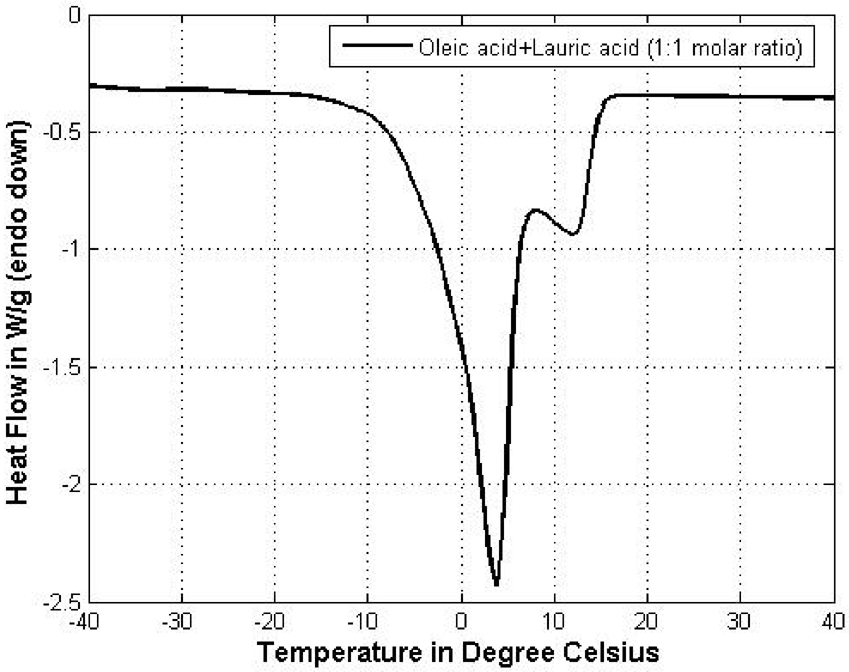


Figure 5.4: DSC Thermogram of the mixture of oleic acid and lauric acid

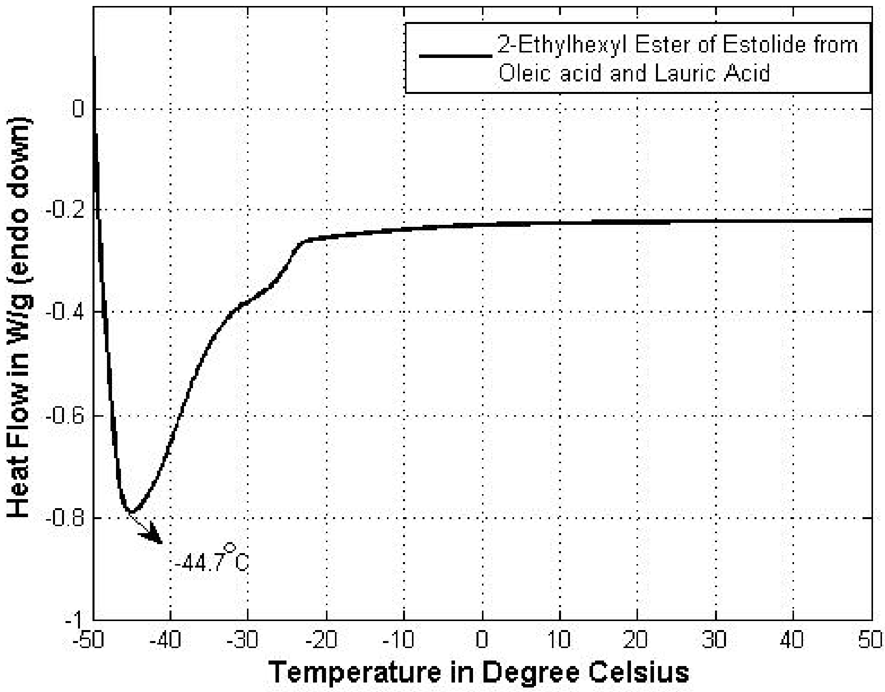


Figure 5.5: 2-ehtylhexyl ester of estolide from oleic acid and lauric acid

DSC thermogram of chemically modified coconut oil (from coconut oil and castor oil-Section 5.2.1a) is shown in Figure. 5.3. The thermogram clearly indicates two predominant peaks; one at 5ºC and the second at -22ºC. The DSC thermogram of the mixture of 90%

coconut oil and 10% castor oil (the vegetable oil constituents of the reactant mixture as explained in Section 5.2.1) is shown in Figure 5.2 for comparison. The esterification with 2-ethylhexyl alcohol may result in 2-ethylhexyl esters of lauric acid, oleic acid, and other fatty acid constituents of coconut oil, ricinoleic acid (from castor oil), and the estolides formed. Esters of saturated fatty acids (lauric, palmitic and stearic) have comparatively higher melting points (Cermak and Isbell, 2003) causing the endothermic peak at 5ºC. Melting points of 2-ethylhexyl esters of oleic acid and the estolides show excellent cold flow behaviour with pour point less than -30ºC (Isbell *et al.*, 2001; Cermak and Isbell, 2003). The esters of oleic acid and the estolides formed can be the reason for the second peak at -22ºC. The pour point of the product (BB) determined by the ASTM D97 method was -3ºC. The pour point of the product (-3ºC by ASTM D97 method) shows a significant improvement over the unmodified coconut oil (24ºC) and mixture of 90% coconut oil and 10% castor oil (24 ºC). Addition of 10% castor oil (in the reactant mixture) does not cause any significant change in the melting behaviour of coconut oil as is evident from the DSC thermogram shown in Figure 5.3.

The DSC thermogram of the product with reactant mixture of lauric acid and oleic acid (Section 5.2.1b) showed a unique peak at approximately -44.7 ºC and the corresponding pour point as per ASTM D97 method was -42 ºC. DSC thermogram of the reactant mixture is shown in Figure 5.4. It shows two unique endothermic peaks on at approximately 5 ºC and the other above 10 ºC. These peaks correspond to oleic acid and lauric acid respectively.

FTIR and NMR spectroscopic examination confirms the ester functionality in the product. Figure 5.6 shows FTIR spectrum of lauric acid and oleic acid mixture (reactants). The characteristic peak at 1707 /cm and the diffuse peak to the left of 3003/cm are indicative of fatty acid structure in the reactants. The peak at 1736 /cm in the IR spectrum (Figure 5.7) of the product of synthesis is indicative of the ester functionality (2-ethylhexyl ester). The multiplet from 2.25-2.35 ppm in the ^{1}HNMR spectrum (Figure 5.8) indicates α-carbonyl methylene protons (Cermak and Isbell, 2003). The peaks near 173 ppm in the ^{13}CNMR spectrum also suggest ester linkages in the product (Figure 5.9). Since the product is a mixture of fatty acid esters and estolide ester, the structure elucidation requires separation of the products. However, for the use as base oil for lubricants the properties of the mixture are of interest.

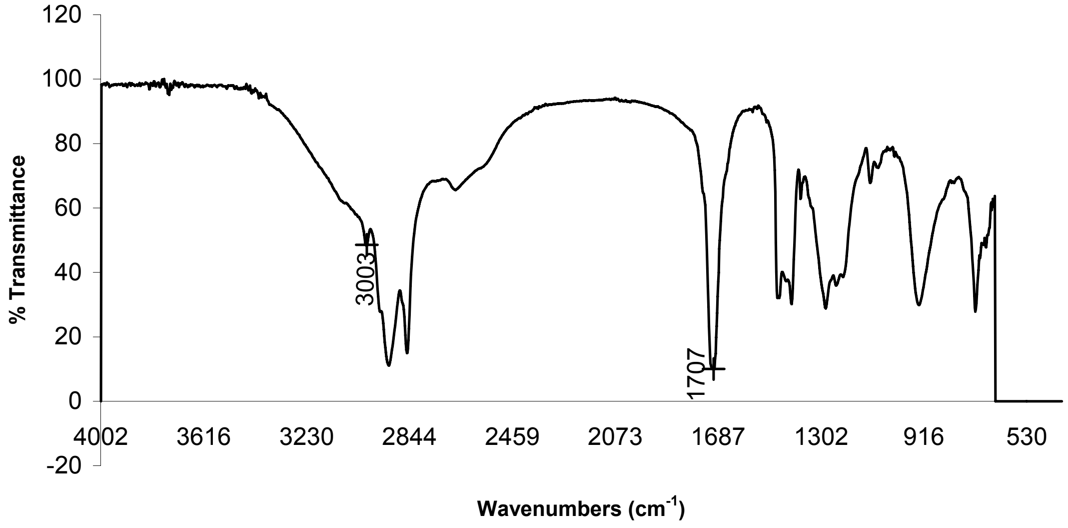


Figure 5.6: FTIR spectrum of lauric acid/ oleic acid mixture

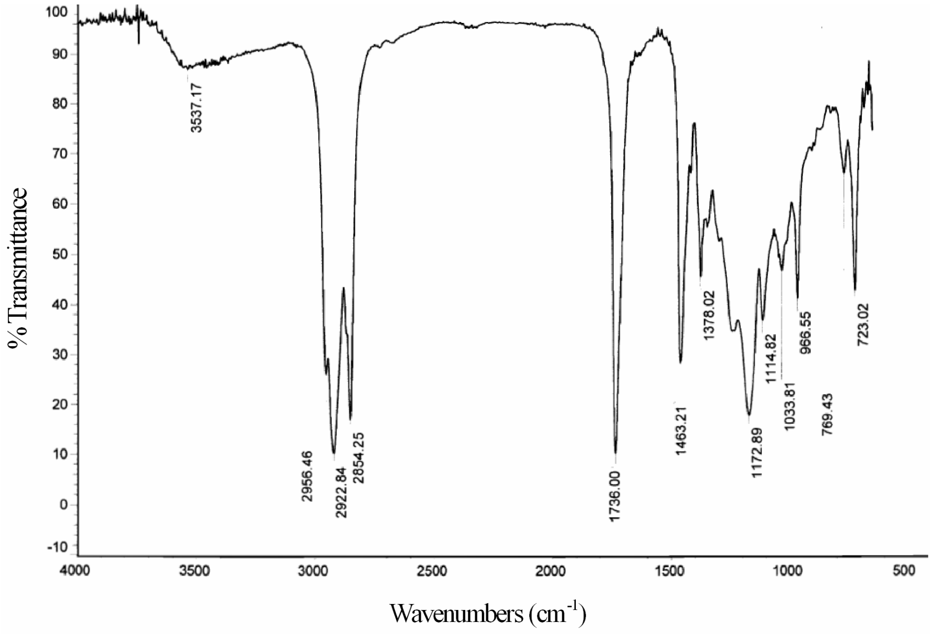


Figure 5.7: FTIR spectrum of 2-ethylhexyl ester of lauric acid/ oleic acid estolide

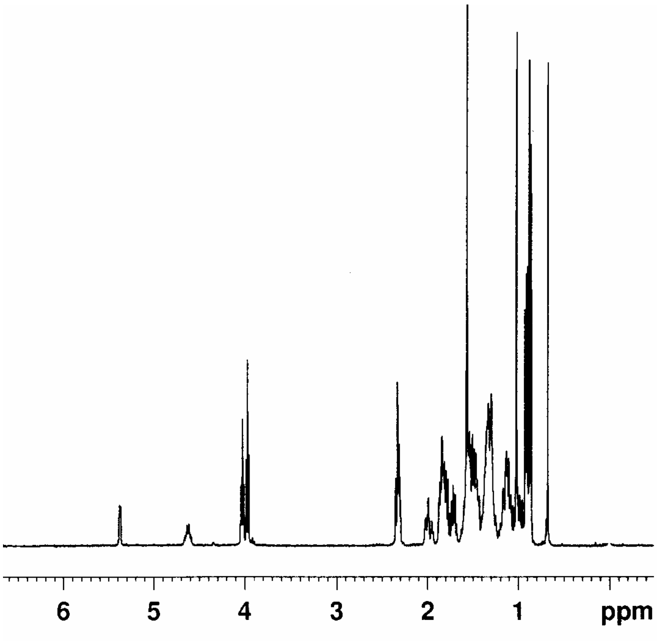


Figure 5.8: ^{1}HNMR spectrum of 2-ethylhexyl ester of lauric acid/ oleic acid estolide

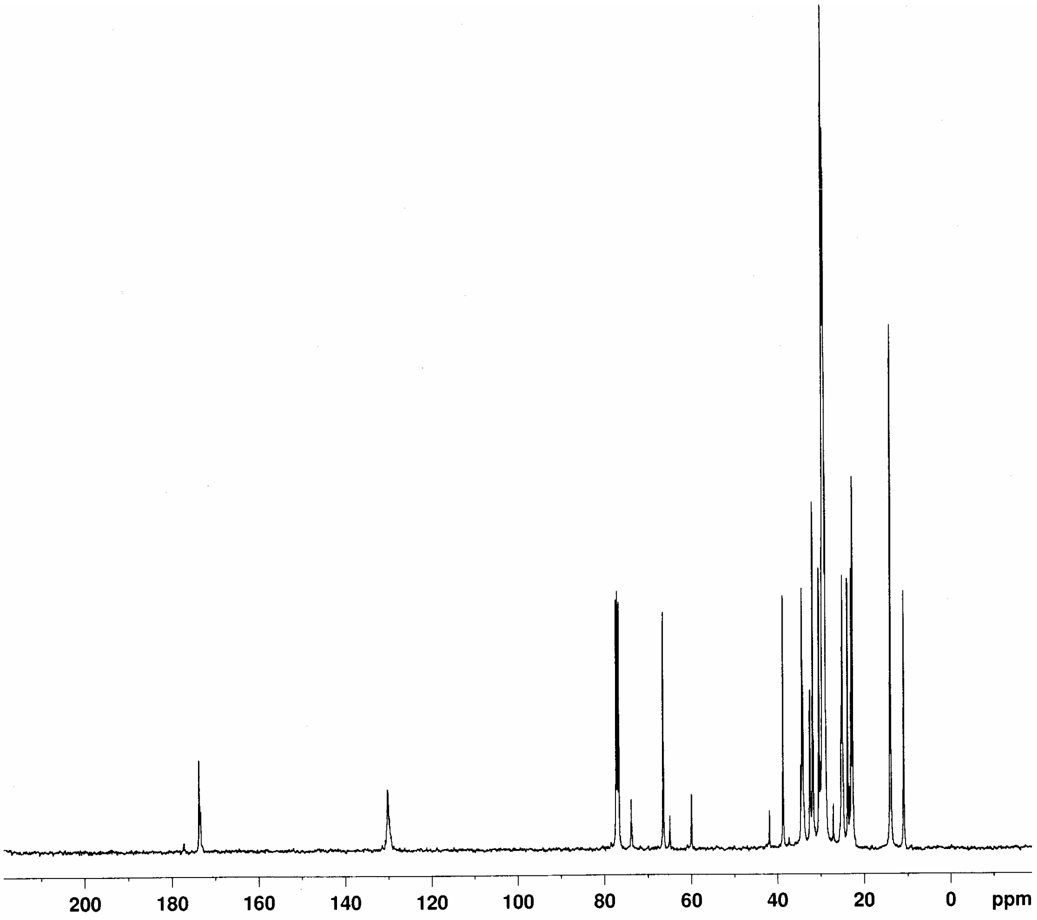


Figure 5.9: ^{13}CNMR spectrum of 2-ethylhexyl ester of lauric acid/ oleic acid estolide

Estolide formation is based on the double bond sites in triacylglycerols. Since coconut oil is predominantly saturated, the double bond sites for reaction are very low in number. To add more double bond sites for estolide formation 10% (by wt.), castor oil was included in the reactant mixture (a). For increased formation of estolide and further reduction of pour point, reactant mixture (b) was used. Estolide formation results from acylation at the double bond cite. If the fatty acid chain added at the double bond site is unsaturated further acylation is possible.

5.4 Conclusions

Coconut oil shows very high pour point (24ºC) compared to other vegetable oils studied (Chapter 3). Chemical modification by acid catalysed condensation reaction with coconut oil castor oil mixture (Section 5.2.1-a) resulted in significant reduction of pour point (from 24 ºC to -3 ºC). Instead of using triacylglycerols when their fatty acid derivatives (lauric acid- the major fatty acid content of coconut oil and oleic acid- the major fatty acid constituents of mono- and poly- unsaturated vegetable oils like olive oil, sunflower oil etc.) were used for the synthesis (Section 5.2.1-b) the pour point could be brought down to -42 ºC. Since the coconut oil has low unsaturated fatty acid content, the unsaturated fatty acid constituents should be obtained from other mono- and poly- unsaturated vegetable oils.

Chapter 6

Evaluation of the lubricant properties of Esterified Estolide

6.1 Introduction

The major limitations in the use of vegetable oils as lubricant base stocks as discussed in Chapter 1 were , poor cold flow properties, poor oxidative stability and deterioration of antiwear and extreme pressure properties at elevated temperatures. To improve cold flow properties, many modification procedures including addition of additives (PPD) and chemical modification techniques like interesterification and synthesis of esterified estolides from vegetable oil fatty acids were tried. 2-ethylhexyl esters of fatty acid estolides synthesized as described in chapter 5 showed excellent cold flow properties. Before recommending this product as a lubricant base stock it should be evaluated for other important lubricant properties like physicochemical, viscometric (viscosity and viscosity index), tribological, oxidative and corrosion properties. This chapter reports the results of the evaluation of the above properties of the 2-ethylhexl estolide ester.

6.2 Physicochemical and Viscometric Properties

Physicochemical and viscometric properties were evaluated as per the relevant ASTM or AOCS standards. The test results are shown in table 6.1.

Table 6.1: Physicochemicall and viscometric properties of 2-ethylhexyl estolide ester

Property	**Values**	**Method**
Pour Point	-42˚C	ASTM D97
Flash Point	194˚C	ASTM D92
Specific Gravity	0.917 (at 20˚C)	ASTM D1217
Viscosity	34.9 cSt (at 40˚C) 7.2 cSt (at 100˚C)	ASTM D445
Viscosity Index	178	ASTM D2270
Iodine Value	3-7	ASTM D1959-97
Acid number	0.1	ASTM D664-04
Peroxide Value	0.5 (max)	AOCS- Cd 8–53

6.3 Oxidative Stability

6.3.1 Thermogravimetric/Differential Thermal Analysis (TGA/DTA)

Vegetable oils especially poly-unsaturated oils are known to possess low oxidative stability (Zeman *et al.*, 1995; Adhvaryu and Erhan, 2002). The properties of vegetable oils are determined by their fatty acid composition. A high content of linoleic/linolenic acid decreases thermal and oxidative stabilities.

Fundamental knowledge of the oxidative properties of lubricants is necessary to predict the long-term thermal stability of these fluids, which is a critically important lubricant property. Oxidation properties evaluated experimentally are often used to predict actual lubricant service life in high temperature and other extreme applications. The more resistant a lubricant is to oxidation, less is the tendency it has to form deposits, sludge, and corrosive by-products in grease, engine oil and industrial oil applications. It is also more resistant to undesirable viscosity increases during use. Igarashi (1990) has discussed various chemical reaction mechanisms based on free radicals, which are thought to be involved in the oxidative degradation of engine oils. The ASTM D943 test method is very widely used in industry to assess storage and long-term service oxidation stability of oils in the presence of oxygen, water, copper and iron at an elevated temperature (95 °C).

In developing new lubricants, it is not usually possible to screen a large number of base oils and anti-oxidant quantity by running expensive and time-consuming performance tests using mechanical hardware. For these reasons, it has become necessary to seek development of new oxidation stability tests, which are capable of representing field performance within a short testing time. Actually, thermoanalytical methods such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have received considerable attention (Dweck and Sampaio, 2004; Santos *et al.*, 2004). These methods are advantageous in relation to the conventional ones because they provide a higher precision and sensitivity as well as use smaller amount of sample and the results are obtained faster. Though TGA and DTA are extensively used for analyzing the thermal and oxidative stabilities of edible oils, these methods are so far not regularly used for the analysis of base oil for lubricants.

Thermogravimetric analysis (TGA) provides the analyst with a quantitative measurement of any change associated with a transition. For example, TGA can directly record the loss in weight with time or temperature due to dehydration and decomposition. Thermogravimetric traces (thermograms) are characteristic of a given compound or system because of the unique sequence of physicochemical reactions that occur over definite temperature ranges and at rates that are a function of molecular structure (Merrit and Settle, 1986). Changes in weight are a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to evolution of volatile products or the formation of heavier reaction products. In differential thermal analysis (DTA), the temperature of a sample and a thermally inert material are measured as a function of temperature (usually sample temperature). Any transition which the sample undergoes will result in liberation or absorption of energy by the sample with corresponding deviation of its temperature from the reference. The differential temperature (ΔT) versus the programmed temperature (T) at which the whole system is being changed tells the analyst of the temperature of transitions and whether the transition is exothermic or endothermic. In isothermal TGA/DTA, the reference temperature remains constant whereas the sample temperature varies according the thermal activities occurring in it.

6.3.2 Oxidative performance of vegetable oils

Most of vegetable oils are triglyceride esters (triacylglycerols) of different fatty acids (FA) with a very few exceptions like jojoba oil (Gunstone, 1999). They are, therefore, complex molecules with different fatty acids attached to a single triglyceride structure. The presence of unsaturation in the triacylglycerols molecule due to C=C from oleic, linoleic and linolenic acid moieties, provides many active sites for various oxidation reactions. Saturated fatty acids have relatively high oxidation stability (Brodnitz, 1968)**,** which decreases with increasing unsaturation in the molecule. Unsaturated oils react with oxygen through a free radical process to form hydroperoxides, which in turn decompose and then crosslink to form polymeric gels. This process is called autoxidation and has been covered thoroughly in reviews (Russell, 1959; Porter *et al.*, 1995). Weight changes are a measurable and an inevitable consequence of the autoxidation processes. Oxygen uptake increases the weight of the oil, as hydroperoxides are formed while bond cleavage produces volatile oxidation byproducts such as carbon dioxide, and short chain acids, aldehydes, ketones, and alcohols. These diffuse out, volatilize, and decrease the weight (Hancock and Leeves, 1989). The measured weight changes represent the net change in weight of the oil film due to oxygen uptake during the free radical and polymerization process and the diffusion and loss of volatiles created by oxidation and molecular rearrangements.

6.3.3 Oxidative Stability Test by TGA/DTA

Oxidative stability of 2-ethylhexyl estolide was tested using the TGA/DTA method as described in Jayadas (2008). In this method the sample is heated to 150 ºC under nitrogen atmosphere. When the temperature reaches 150 ºC, oxygen is turned on (@ 200 ml/minute) and nitrogen is switched off. The sample is held under these conditions for 3 hours. During this period the sample uptakes oxygen and undergoes oxidative reaction. The weight changes and exothermic heat flows are continuously monitored during this period. Vegetable oils undergo significant weight changes during this period due to oxidative reactions. The exothermic heat flows as recorded in the process is indicative of the extent of the reactions.

Table 6.2 shows the tabulated result of the TGA/DTA analysis of coconut oil (a predominantly saturated oil), sunflower oil (a poly-unsaturated oil), 2-ethylhexyl estolide ester (the sample under study) and a commercial lubricant of SAE 20W50 grade. Figures 6.1 (normalized weight changes) and 6.2 (heat flows) show TGA/DTA traces of the oils tested. Oxygen uptake and formation of peroxides cause an initial weight gain in unsaturated and polyunsaturated oils (Jayadas, 2008). Weight gain for different oils tested is shown in percentage in Table 6.2, column 2 (W_{gain}). For all oils except sunflower oil the weight gain during the test period is zero, indicating absence or slow oxidative reactions.

The 3rd column shows the value of heat flow (H_{exo}). Negative values show heat flow into the samples. As purge gases (oxygen in the present cases) takes away heat from the sample, heat is to be continuously supplied to sample to maintain the constant temperature (in isothermal tests) and the values of H_{exo} in the absence of any chemical reaction is proportional to the heat capacity of the respective oils. Figure 6.2 shows clear evidence of thermal activity in coconut oil and sunflower oil. Due to saturated nature of coconut oil fatty acids, the thermal activity in coconut oil is comparatively lesser than in sunflower oil. 2-ethylhexyl estolide ester shows very little thermal activity during the test period similar to the commercial SAE 20W50 oil.

The oil samples depending on the degree of unsaturation initially gain weight due to oxidative polymerization and then decompose into ketones, aldehydes and alcohols which are volatile and hence get eliminated by evaporation. T_{onset} is the time at which 2% weight loss occurs. The values of T_{onset} shown in column 4 of Table 6.1 show that 2-ethylhexyl estolide ester is least prone to weight loss as a result of continued heating and hence is most stable among the oils tested.

Table 6.2: Oxidative characteristics of the tested oils from TGA/DTA

Oils	W_{gain} **in %**	H_{exo} **W/g**	T_{onset} **min**
Coconut oil	0	-0.858	94.3
Sunflower oil	0.77	0.716	21.9
2-ethylhexyl estolide ester	0	-1.132	>180
Commercial SAE 20W50 oil	0	-1.459	41.87

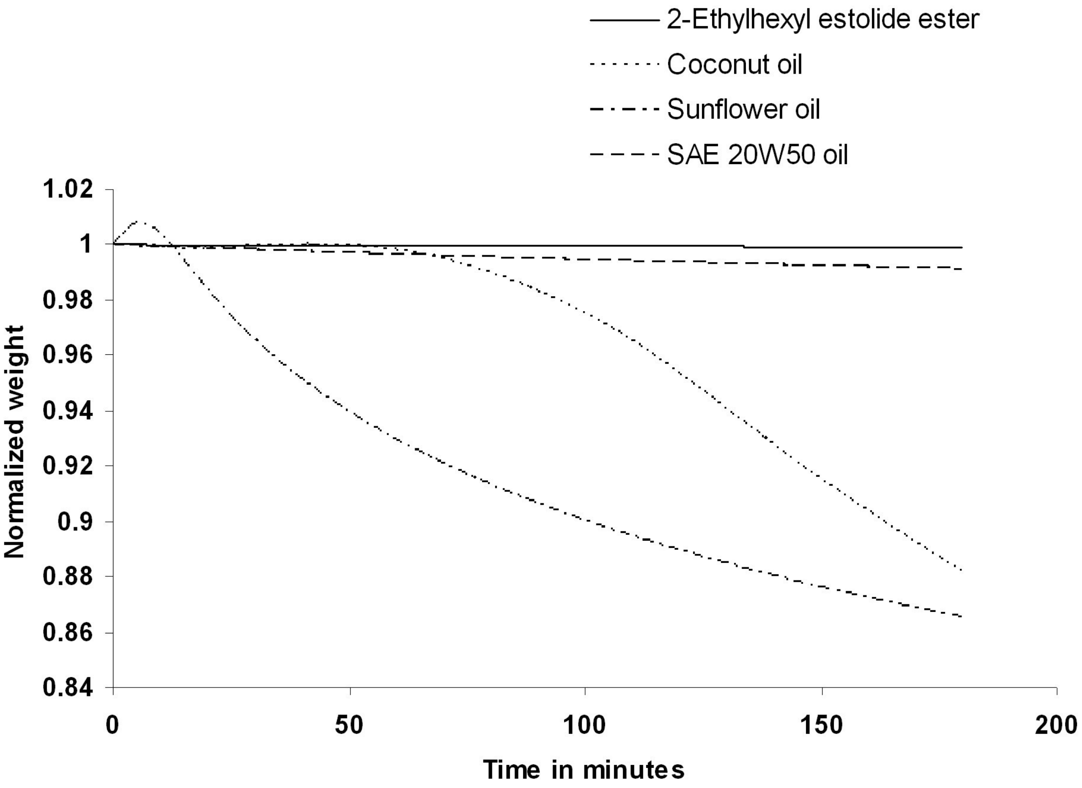


Figure 6.1: Normalized TGA trace at 150 ° C

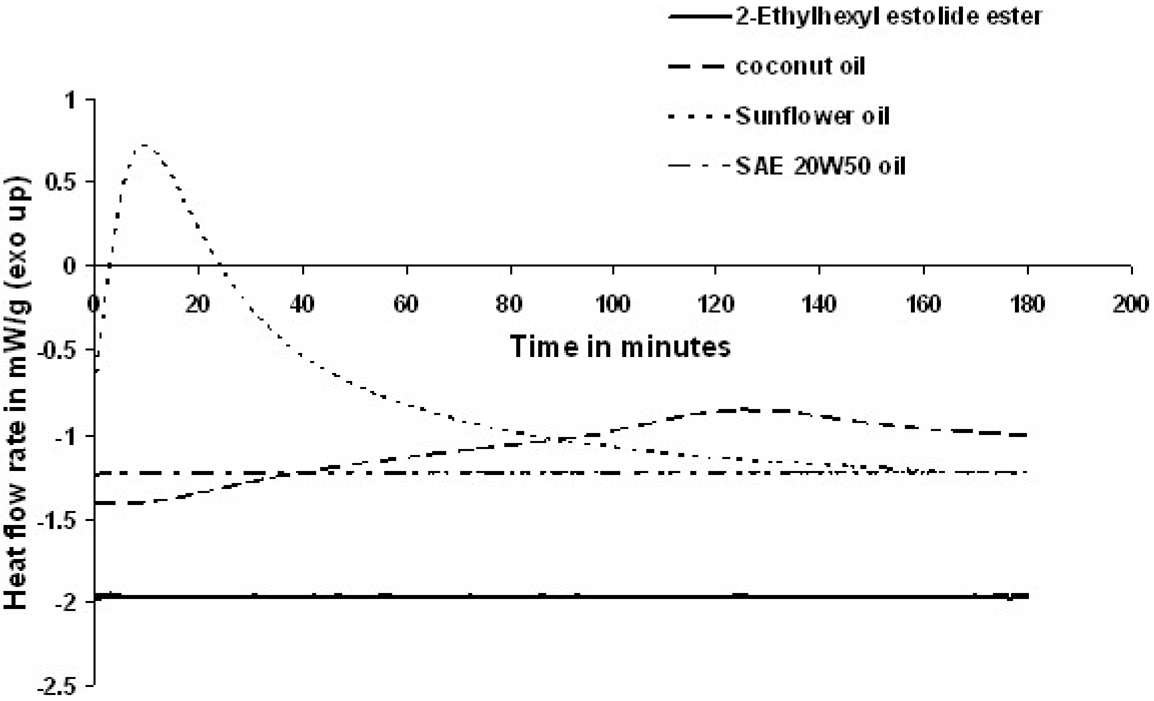


Figure 6.2: Normalized DTA trace at 150 ° C

6.4 Tribological Properties

Vegetable oils are very good boundary lubricants in that they give rise to very low coefficient of friction (μ). At the same time, many researchers report that even while the coefficient of friction is low with vegetable oil as a boundary lubricant, the wear rate is high (Bowden and Tabor, 2001). It is possible that this behaviour is due to the chemical attack of the surface by the fatty acid. On this view, the metallic soap film is rubbed away during sliding and is continuously reformed by further chemical reaction. Non-reactive detergents may also produce a similar increase in wear and suggests that the additive removes, by a detergent action, the detritus on the surface, which otherwise would act as a protective film (Bowden and Tabor, 2001).

The tribological properties of estolide were evaluated using a four-ball tester as per ASTM D4172 method. The influence of an anti-wear/extreme pressure (AW/EP) additive on the tribological performance of coconut oil and optimum additive concentration was also evaluated experimentally.

Zinc dialkyldithiophosphate (ZDDP) was selected as the AW/EP additive for the present study because of the following reasons (Plaza and Kajdas, 1994; Barnes *et al.*, 2001; Spikes, 2004; Nicholls *et al.*, 2005).

1) ZDDP is the most widely used AW/EP additive in the industry.

2) The decomposition and anti-wear mechanisms of ZDDP have been well studied.

3) ZDDP is a multifunctional additive. ZDDP can also be used as an anti-oxidant and a corrosion inhibitor.

6.4.1 Tribological Tests on Four-Ball Tester

Anti-wear and extreme pressure tests on coconut oil had been conducted using a four-ball tester TR 30L, DUCOM, Bangalore, India as per ASTM D4172 and ASTM D2783 respectively. For comparison, the tests were repeated on a commercial lubricant SAE 20W50. To improve the tribological properties of coconut oil, an AW/EP additive zinc dialkyldithiophosphate (ZDDP) was added to coconut oil. To determine the optimum additive (AW/EP) concentration, the wear tests (ASTM D4172) were performed at different additive concentrations (% weight).

Wear scar diameter (WSD) was measured using an optical microscope with a resolution of 0.01 mm (as per ASTM D4172) and the coefficient of friction (μ) was calculated from the average tangential load as indicated by the machine. Wear scar diameters were calculated strictly in accordance with the ASTM D4172 procedure. The frictional torque for the calculation of the tangential load was obtained from a load cell (with ±0.01Nm accuracy) and a computerized data acquisition system. The average tangential load was calculated from the values of frictional torque sampled at 30 readings per minute. The coefficient of friction was then computed from the average tangential load and the normal load (392 N, least count of the machine: ±1N), applied as per ASTM D4172 method. The values of the coefficient of friction calculated as described above (and returned by the computer) were rounded to two decimal digits. The additive-added coconut oil was then tested for the extreme pressure performance on the four-ball tester as per ASTM D2783. The weld loads (the load at which the rotating ball seizes and welds to the stationary balls) are reported in Newton (±1 N) as per ASTM D2783. Each test had been repeated three times and average values were taken.

The results of the tribological evaluation of the product i.e. 2-ethylhexyl estolide ester, are shown in Table 6.3. The values of the coefficient of friction (**μ**)**,** wear scar diameter and weld load of the product are poorer compared to the SAE 20W50 oil tested for comparison.

Table 6.3: Coefficient of friction and wear scar diameters of test oils determined as per ASTM D4172 and weld load determined as per ASTM D2783

Oil	Coefficient of friction (μ)	Wear scar diameter (mm)	Weld load (N)[a]
2-ethylhexyl Estolide Ester	$0.11^{+0.01}_{-0.01}$	$0.71^{+0.05}_{-0.03}$	1236
SAE 20W50	$0.08^{+0.01}_{-0.01}$	$0.36^{+0.03}_{-0.03}$	1962
Estolide+2% AW/EP additive	$0.07^{+0.01}_{-0.01}$	$0.38^{+0.04}_{-0.03}$	2453

[a] Loads are applied for weld test in steps 981 N, 1236 N, 1962 N etc.

To improve the tribological performance 2% zincdialkyldithiophosphate (ZDDP) was added to the product. The values of the coefficient of friction (**μ),** wear scar diameter and weld load of the product with 2% ZDDP compare favorable or even better than that of the commercial 20W50 oil.

6.5 Anti-Corrosion Characteristics

Vegetable oil undergoes hydrolysis in the presence of moisture leading to the formation of free fatty acids. The COOH head groups of fatty acids are hydrophilic in nature and hence attract water molecules. Because of their polarity, the COOH head groups get attracted to the metallic surfaces and adsorb on them. This process leads to increased corrosion of metallic surface due the hydrophilicity of polar heads of the fatty acid molecules adsorbed on metallic surfaces. Being an ester, 2-ethylhexyl estolide ester is also susceptible to hydrolysis and hence increased corrosion.

The sample is tested for corrosion characteristics by copper strip corrosion test, (ASTM D130) and rust prevention characteristics test (ASTM D665). The test was repeated with 1% zinc dialkyldithio-phosphate (ZDDP) as an anti corrosive agent (Jayadas and Nair, 2007). The results are shown in Table 6.4. The sample passed the copper strip corrosion test (1/a) and failed in the rust prevention test. Sample with 1% ZDDP passed the rust prevention test.

Table 6.4: Corrosion test results on 2-ethyhexyl estolide ester without and with additive

Oil	Copper strip test (ASTM D130)	Rust prevention Characteristics test ASTM D665
2-ethylhexyl estolide ester	1/a	fail
2-ethylhexyl estolide ester+1% ZDDP	1/a	pass

6.6 Conclusions

The viscometric properties of 2-ethylhexyl estolide ester i.e. the kinematic viscosities at 40 ºC (34.9 cSt) and 100 ºC (7.2 cSt) indicate that the product is suitable for two-stroke engine application (as a total loss lubricant). It has an exceptionally good viscosity index value of 178 and flash point of 194 ºC. Oxidative performance of the product was comparable to or better then that of the SAE 20W50 oil tested for comparison. Tribological tests by the standard antiwear test (ASTM 4192) and extreme pressure test (ASTM D2783) of the product with 2% ZDDP showed excellent antiwear characteristics. The sample passed the copper strip corrosion test (ASDTM D130) and failed in the rust prevention test (ASTM D665). Sample with 1% ZDDP passed the rust prevention test.

Chapter 7

Summary and Conclusions

7.1 Summary

Vegetable oils are perceived to be alternatives to mineral oils as base oils for industrial lubricants due to growing environmental concerns. Vegetable oil based lubricants offer significant environmental benefits with respect to resource renewability, biodegradability, low toxicity, and provide satisfactory performance in a wide array of applications. Vegetable oils in general have excellent properties such as high viscosity index, high lubricity, high flash point, and low evaporative loss with regard to their use as base oils for lubricants. On the negative side, they are known to possess low thermal, oxidative and hydrolytic stabilities and poor low temperature characteristics. Vegetable oils are also found to be temperature sensitive in the case of tribological properties especially at high temperatures. Some of the important base oil properties of industrial lubricants are viscometric, physico-chemical, tribological, oxidative, thermal, hydrolytic, corrosion and low temperature properties. The present day mineral oil lubricants consist of a base oil (>90%) and an additive package (<10%) to enhance its lubricant properties. Recent literature reports development of novel additives and chemical modification processes to improve the oxidative and hydrolytic stabilities of vegetable oils to make them suitable as base oils. Literature survey also reveals many chemical modification processes suitable for vegetable oils to improve their base oil properties including cold flow characteristics.

The poor cold flow properties of vegetable oils can be attributed to their unique molecular structure, namely, triacylglycerol structure. Vegetable oils have a tendency to form macro crystalline structures at low temperature through uniform stacking of ‘bend’ triacylglycerol backbone. Such macro crystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self stacking. The predominantly saturated fatty acid content of certain tropical oils like coconut oil compounds the problem further. This is attributed to close packing of the saturated fatty acid chains in triacylglycerols during cooling forming crystals which entrap the low melting constituents leading the formation of gels (congelation). Attachment of side chains at double bond positions by chemical modification procedures like oligomerization (synthesis of dimers, estolides etc.) and alkoxylation is suggested as possible methods to improve cold flow behaviour of vegetable oils. Conventional method for determining pour point is ASTM D97 method. ASTM D97 method is time consuming and reproducibility of pour point temperatures is poor between laboratories. Differential Scanning Calorimetry (DSC) is a fast, accurate and reproducible method to analyze the thermal activities during cooling/heating of an oil.

In the present work coconut oil is chosen as representative vegetable oil for the analysis and improvement of cold flow properties since it is abundantly available in the tropics and has a very high pour point of 24 °C. DSC is used for the analysis of unmodified and modified vegetable oil. To modify cold flow properties different techniques like additive-addition and chemical modifications were carried out. The modified oils were analyzed by DSC to ascertain the effectiveness of the procedures adopted. Since poor pour point (high) was the major hurdle in the use of vegetable oils as lubricants, the first task was to bring down the pour point to desired level. The modified oils (with acceptable pour points) were then subjected to different tests for the valuation important lubricant properties like viscometric, tribological (friction and wear properties), oxidative and corrosion properties.

Interestification of coconut oil with other vegetable such as castor oil, sunflower oil and keranja oil was attempted to reduce pour point of coconut oil. Refined coconut oil and other oils like castor oil, sunflower oil and keranja oil were mixed in a round bottomed flask in different proportions. The flask with the mixture was placed on a heater with magnetic stirring attachment. A magnet was dipped in the oil mixture for stirring purpose. The mixture was heated at a constant temperature of 180^{o}C, for 1 hour with continuous stirring. After 1 hour, any moisture content in the flask was removed by vacuum pump. Sodium metal (Na) was added to the mixture as catalyst. Sodium was added in catalytic proportions (1% by weight). Heating and stirring was continued again up to 3 hours. Then the mixture was cooled to room temperature and filtered by filter paper. All the reactions were done at atmospheric pressure.

A commercial polymethacrylate based PPD (obtained from Lubrizol, Chennai, India) was added in different percentages (by weight) from 0.1 to 0.5 and the pour points were determined in each case. Styrenated phenol (SP) has a complex 3-dimensional structure, which can hinder the formation of large fat crystals during solidification. SP was added in different concentrations to coconut oil and each solution was subjected to ASTM D97 test and analysis by DSC.

The acid catalyzed condensation reactions were conducted without solvent in a 500 ml, baffled, jacketed reactor with a three-neck reaction kettle cover. The reactor was connected to a recirculating constant temperature bath maintained at 60±0.1°C. An overhead stirrer using a Teflon coated shaft and a Teflon blade was used for mixing. The reactions were conducted at atmospheric pressure. The reaction was carried out with two reactant mixture a) reactant mixture containing coconut oil, castor oil, and oleic acid and b) a reactant mixture containing lauric acid and oleic acid.

The reactant mixture was heated to 60°C with overhead stirring. Once the desired temperature was reached, a catalytic quantity of perchloric acid ($HClO_4$) was added drop wise to the mixture and the reaction vessel was stoppered. After 24 hours, 2-ethylhexyl alcohol was added to the vessel and the mixture was stirred for 2 additional hours. The completed reactions were quenched by the addition of potassium hydroxide (KOH) (1.2 equivalents based on $HClO_4$) in 90% ethanol water solution. The solution was allowed to cool for 30 minutes. The organic layer was extracted with hexane and dried over sodium sulphate and concentrated *in vacuo*. Coconut oil used was commercially available edible grade oil. Oleic acid, castor oil, perchloric acid, 2-ethylhexyl alcohol, and potassium hydroxide were laboratory grade reagents obtained from Aldrich.

7.2 Conclusions

Vegetable oils solidify at higher temperatures than the pour points determined by the ASTM D97 method on prolonged storage at low temperature. At the cooling rate as employed in ASTM method, vegetable oils crystallize in to low melting α polymorph which on prolonged storage re-crystallizes in to higher melting polymorphs β and β'. DSC thermogram captures the thermal activities (melting, crystallization etc.) in vegetable oils as they are heated or cooled at different rates. Cooling thermograms are rate dependent whereas heating thermograms are independent of heating rate as far as position of peaks (crystallization or melting) are concerned. Hence, DSC (heating) was proven to be an ideal tool for analyzing the low temperature properties of vegetable oils.

The effect of PPD on the pour point of coconut oil was not significant. Addition of SP caused significant reduction of pour point from 24 °C (0% SP) to 12°C (15% SP). But the pour point obtained was still much higher than that is required for any lubricant application (-6°C for two-stroke engine lubricant as per IS14234). Coconut oil due to the predominantly saturated nature of its fatty acids has very high pour points.

Interesterification with other vegetable oils was not found to be very effective in lowering the pour point of coconut oil as the reduction attained was only to the extend of 2-3

°C. DSC analysis has shown that there is always a peak corresponding to the solidification of the triacylglycerol molecules with predominantly saturated fatty acid content (lauric acid). The wax formation at high temperature may lead to other low melting components leading to the formation of gel like structure.

The DSC thermogram of chemically modified coconut oil clearly indicates two predominant peaks; one at 5ºC and the second at -22ºC. Melting points of 2-ethylhexyl esters of oleic acid and the estolides show excellent cold flow behaviour with pour point less than -30ºC [15,17]. The esters of oleic acid and the estolides formed can be the reason for the second peak at -22ºC. The pour point of the product (BB) determined by the ASTM D97 method was -3ºC. The pour point of the product (-3ºC by ASTM D97 method) shows a significant improvement over the unmodified coconut oil (24ºC) and mixture of 90% coconut oil and 10% castor oil (24 ºC). The DSC thermogram of the product with reactant mixture (b) indicates that the pour point is -42 ºC. FTIR and NMR spectra of the product showed no indication of un-saturation which is good for better oxidative stability. Presence of un-saturation is the major reason for the poor oxidative stability of natural oils. FTIR and NMR spectroscopy confirmed the ester structure of the product which is fundamental to the biodegradability of vegetable oils.

The tribological performance with a suitable AW/EP additive was comparable to the commercial SAE20W30 oil. The viscometric properties (viscosity and viscosity index) were also (with out additives) comparable to commercial lubricants. The TGA experiment confirmed the better oxidative performance of the product compared to other vegetable oils. The sample passed corrosion test as per ASTM D130 method.

7.3 Limitations

Synthesis procedure adopted in this work was done on a laboratory scale. The product synthesized with vegetable oils (coconut oil and castor oil) as starting material showed a pour point value of -3°C. Though the reduction in pour point was significant (from 24 °C to -3°C), it is not sufficient for most applications. The product which showed excellent cold flow properties with pour point at -42°C was synthesized using commercially available fatty acid constituents. Using commercial fatty acids for the synthesis of esterified estolides as base stocks for lubricants is economically not feasible. The product of synthesis was a mixture of esters of estolide and un-reacted fatty acids. The latter was removed by vacuum distillation which is time consuming and costly. This procedure reduced the yield considerably which could prove to be a major hurdle in commercial production. TGA method was used for the study of oxidative performance which is not a standard method approved by ASTM. All other lubricant tests were done strictly according to the relevant ASTM standards.

7.4 Further Work

The synthesis of the successful sample has been obtained by using the laboratory grade fatty acids. A direction for further work would be to devise a process to derive estolide esters directly from vegetable oils with the production of fatty acids as the initial step. Vegetable oil fatty acid can be produced from the vegetable oils by hydrolysis with or without catalysts like using acid/base catalysis or by using high pressure steam. If the production of the fatty acid is incorporated as the initial step followed by the synthesis of estolides, the production can be done in a continuous mode with high yield. Further research may be directed for the design of suitable reactors for continuous production of fatty acids and subsequent synthesis of esterified esters.

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Appendix 1

Publications

International Journals

1. N. H Jayadas, K Prabhakaran Nair and G Ajithkumar,2007, Tribological evaluation of coconut oil as an environment-friendly lubricant , Tribology International ,Vol.40,pp. 350-354
2. G. Ajithkumar, M. Bhasi and N. H Jayadas, 2008, Analysis of the Pour Point of Coconut Oil as a Lubricant Base Stock using Differential Scanning Calorimetry, Lubrication Science, Wiley InterScience, Vol.21 ,pp.13-26

International Conferences:

1. N H Jayadas, K Prabhakaran Nair, G Ajithkumar, 2004,Coconut oil as Bio Lubricant - Evaluation of the Tribological Properties, Proceedings Ist International Conference on advanced Tribology, iCAT 2004, NUS Singapore
2. N H Jayadas, K Prabhakaran Nair, G Ajithkumar, 2005, Vegetable Oils as Base Oil for Industrial Lubricants- Evaluation of Thermal, Oxidative and Low Temperature Properties Proceedings World Tribology Congress 2005, WTC 2005, ASME
3. G. Ajithkumar, M. Bhasi and N H Jayadas, 2008, Titles Analysis of the Cold Flow Properties of Additive-added and Chemically Modified Coconut Oil Using Differential Scanning Calorimetry (DSC), Proceedings ICICAME 2008, IISc Centenary-Internatinal Conference on Advances in Mechanical Engineering, IISc Bangalore, 2-4 July 2008

National Journals

1. Jayadas, N. H., Ajithkumar, G., and Saju, K. K., 2003, “Coconut Oil as an Alternative to Automobile Lubricants,” Indian Coconut Journal, **34**(5), pp. 3-7.

Appendix 2

Biodata

1) Name: G.Ajithkumar

2) Affiliation: Cochin University of Science & Technology

3) Date of Birth: 01-06-1965

4) Research Interests: Tribology, Vegetable Oil based Lubricants

5) Academic Background:

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1	B Tech	Mechanical Engineering	Kerala University	1987
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Appendix 3

Details of Instruments Used in this Work

1. Thermo Gravimetric Analyser

Specifications

Make/Model: Perkin Elmer, Diamond TG/DTA

Temperature range: Ambient – 1200°C

TG Measurement Range: 200 mg

TG Sensitivity: 0.2 mg

DTA measurement Range: ±1000mV

DTA Sensitivity: 0.06mV

Programmable rate: 0.01 – 100°C / min

Sample pan volume: 45ml or 90ml

Atmosphere: Air, inert gas, Oxygen

Pure gas flow rate: 0-1000 ml/min

2. Anti-wear and extreme pressure tests on coconut oil had been conducted using a four-ball tester TR 30L, DUCOM

Specifications

Speed: 1000-3000 RPM

Max axial load: 10,000

Test ball (Diameter): 12.7 mm

Standards

ASTM D2783

ASTM D2596

ASTM D2266

ASTM D4172

3. Diferential Scanning Calorimetry

Specification

Make/Model: Mettler Toledo DSC 822e

Temperature Range: -150 °C to max. 700°C

Measurement range: ± 350 mW at RT

Measurement resolution: 0.04 mW at RT

Temperature Accuracy: ± 0.2°C

Temperature reproducibility: ± 0.1°C

Heating rate: RT to 700°C in 7 min

Cooling rate: + 100°C to - 100°C in 15 min

Sampling rate: Max 10 values / sec