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.
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 predefine 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 150°C 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 ~ -10°C 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 \(~25\) °C. 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 \(\alpha\) 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 \(\alpha\) 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.