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°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 (HClO₄) 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 HClO₄) 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 \textit{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 \( \alpha \) polymorph which on prolonged storage re-crystallizes in to higher melting polymorphs \( \beta \) and \( \beta' \). 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 5°C and the second at -22°C. Melting points of 2-ethylhexyl esters of oleic acid and the estolides show excellent cold flow behaviour with pour point less than -30°C [15,17]. The esters of oleic acid and the estolides formed can be the reason for the second peak at -22°C. The pour point of the product (BB) determined by the ASTM D97 method was -3°C. The pour point of the product (-3°C by ASTM D97 method) shows a significant improvement over the unmodified coconut oil (24°C) and mixture of 90% coconut oil and 10% castor oil (24 °C). 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.