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.

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±0.1°C. 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±0.1°C. An overhead stirrer using a Teflon coated shaft and a Teflon blade was used for mixing. The reactions were conducted at atmospheric pressure. A reactant mixture containing 90g coconut oil, 10g castor oil, and 20.3g oleic acid was used. The reactant mixture was heated to 60°C with overhead stirring. Once the desired temperature was reached, 3g (~0.4 eq., 1.8 mL) perchloric acid (HClO₄) 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 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 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 °C. All the reaction conditions were the same as for reactions carried out in the previous section. Once the desired temp was reached perchloric 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 oil (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-ethylhexyl 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 5°C and the second at -22°C. 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 1HNMR spectrum (Figure 5.8) indicates α-carbonyl methylene protons (Cermak and Isbell, 2003). The peaks near 173 ppm in the 13CNMR 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 (24°C) 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 °C to -3 °C). 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 °C. 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.