Chapter - 6

Overall Summary and Conclusions
Vegetable oil-derived biolubricants are sustainable alternative to the conventional mineral oil lubricants. They are renewable and have several advantageous features. Their use leads to environmental protection. However, the high cost of their production using homogenous mineral acid and Lewis acid catalysts limit their wide spread utility. Application of solid catalysts in place of homogeneous acid catalysts make the manufacturing process economical and eco-friendly as the solid catalysts are reusable and avoid the tedious steps involved in catalyst separation from the product. Among several methods, transesterification of vegetable oils with long-chain alcohols and esterification of fatty acids (products of vegetable oil refining process) with polyols or long-chain alcohols are the most common methods for producing biolubricants. Development of more efficient, stable and robust solid catalysts is a challenging task to make these processes more attractive.

In this thesis, the catalytic application of three new families of solid catalysts (vis., double-metal cyanide (DMC) complexes, titanosilicates and zirconium phenyl phosphonate phosphites) for production of biolubricants has been investigated. Lewis acidity, mesoporosity and hydrophobicity are some common features of these three sets of catalysts. While Lewis acids are the actives sites for esterification/transesterification reactions to occur, mesoporosity enables facile diffusion of bulky reactant and product lipid molecules and enables access to the active sites. Water is the by-product in esterification reaction of fatty acids. Hydrophobicity of catalyst surface makes sure the adsorption of lipid molecules and not water. It is noted that all these catalysts are highly active in producing lubricant base stocks with varying properties suitable of a wide range of applications. In polyol esters synthesis, while DMC catalysts are selective for polyol monoesters formation, titanosilicates and zirconium phenyl phosphonate phosphite catalysts are selective for di- + triesters formation. These catalysts were found reusable in several recycling studies. Main conclusions from different chapters are provided below.

Chapter – 1 provided general introduction to biolubricants. It provided a brief history of various catalysts used in producing biolubricants. Scope and objective of the work were also provided in this chapter.

Chapter - 2 presented the experimental methodologies adopted in this work. It described the procedures for catalysts preparation, characterization, catalytic activity studies and product identification/quantification.
Chapter – 3 discussed the application of solid Fe-Zn double-metal cyanide catalysts for (i) esterification of fatty acids with glycerol and (ii) transesterification of methyl oleate (a component of biodiesel) with long-chain alcohols in batch reactions. DMC catalysts with varying acidities were prepared by synthesizing the material at four different temperatures (10, 25, 50 and 80 °C). The catalyst prepared at 50 °C exhibited highest catalytic activity. At lower reaction temperature (140 °C) and shorter period of time (< 1 h), high selectivity for monoglycerides (83%) was observed over DMC-50 °C catalyst. Water formed as by-product did not deactivate the catalyst as the surface of DMC is hydrophobic.

Synthesis of fatty acid monoesters through the reaction of a fatty acid methyl ester with a long-chain alcohol [2-ethyl-1-hexanol (C₈OH), 1-decanol (C₁₀OH) and 1-dodecanol (C₁₂OH)] using a DMC-50 °C catalyst was investigated. Fatty acid monoesters find applications in synthetic lubricants, paint additives, plasticizers, pharmaceuticals and cosmetics. Most of the known acid catalysts at high temperatures form ethers. Formation of such undesired ether product was not observed even at 200 °C over the DMC catalyst of this work. Fatty monoester of long-chain alcohols was the selective product over DMC. Catalyst reusability study revealed that DMC is a stable and reusable catalyst. Surface area, acidity and hydrophobicity of the catalyst surface are the parameters that influenced the catalytic activity. The product long-chain alcohol esters have the desired physical properties required for lubricant applications.

Chapter – 4 offered the catalytic activity studies of three-dimensional, ordered, mesoporous titanosilicate Ti-SBA-12 and Ti-SBA-16 catalysts in the esterification of oleic acid (OA) with polyhydric alcohols viz., glycerol (G), trimethylolpropane (TMP), neopentylglycol (NG) and pentaerythritol (PE) producing synthetic polyol esters. Ti-SBA-16 (Si/Ti molar ratio = 50) was found superior to Ti-SBA-12 (Si/Ti molar ratio = 40) in the esterification reactions as the former is relatively more hydrophobic than the latter. OA conversion with different polyols decreased in the order: TMP > G > NPG > PE. The influence of reaction parameters in catalytic activity and selectivity was investigated. At an optimum molar ratio of OA : TMP = 3: 1, 180 °C and reaction time of 10 h, di- + trimesters selectivity as high as 98.6 mol% was obtained using Ti-SBA-16 (Si/Ti = 50) catalyst. Fatty acid chain length was found to have an effect on the product selectivity. Longer chain-length acids lead to selective di + trimer products. The titanosilicate catalysts were reusable. The
composition of the polyol esters in the product can be controlled or varied by changing OA to polyol molar ratio, temperature, reaction time and type of catalyst used. Dispersed tetrahedral Ti ions are the acid sites catalyzed the esterification reaction. The physical properties lubricants prepared using Ti-SBA-16 (Si/Ti = 50) catalyst at OA : TMP molar ratio = 4:1, temperature = 180 °C and reaction time = 10 h match with those of commercial lubricants of brand names VP lubricant base oils 700 and 150BS, Servo - gear HP85 and HP90, boat engine oil SAE grade 20W-40, Ultra 40 and 50 and Servo 4T.

Chapter 5 presented the catalytic application of zirconium phenyl phosphonate phosphite (ZrPP) in producing fatty acid polyol esters. ZrPP were prepared with varying phosphorous acid to phenyl phosphonic acid input molar ratio and evaluated as catalysts in esterification reactions of oleic acid with glycerol and TMP. The catalyst with phosphorous acid/phenyl phosphonic acid molar ratio of 3:1 showed high catalytic activity and most importantly the DE + TE selectivity. The influence of process parameters on activity and selectivity of the catalyst was also investigated. With increasing molar ratio of OA/polyol from 0.5 to 4, a decrease in the conversion of OA from 83.0 to 49.0 mol% was observed, while more and more of mono- and diesters got converted into polyol triesters. At OA: polyol molar ratio of 4:1, reaction temperature of 180 °C with reaction time of 1 h, the selectivity for DE + TE was 92.3 mol% for glycerol and 86.0 mol% for TMP. Hydrophobicity of ZrPP and strong acidity are possibly the key features for their high activity and selectivity in polyesterification reactions. ZrPP was reusable in at least three recycling experiments.

By and large, this thesis reported the catalytic application of three different solid acid catalysts viz., 1) Fe-Zn double-metal cyanide (DMC) complexes, 2) Three-dimensional, mesoporous titanosilicates Ti-SBA-12 and Ti-SBA-16, and 3) Zirconium phenyl phosphonate phosphate (ZrPP) complex, for producing vegetable oil-based biolubricant base stock. These catalysts were found stable and superior to the hither to know solid acid catalysts used for these applications. While DMC catalysts were selective for polyol monoesters formation, Ti-SBA-16 and ZrPP were found selective for polyol di- and trimesters formation, respectively. In general, this work contributes to the area of green and sustainable catalytic processes.