

Synopsis

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Title	:	Non-catalytic synthesis of biolubricant esters and their solubilities in supercritical fluids
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Breakdown products released due to increased loss of mineral oil based lubricants to the environment lead to aquatic toxicity and release of harmful volatile compounds into the atmosphere. The production of these conventional mineral oil based lubricants is not sustainable as it is dependent on the fast depleting crude oil sources. The properties of the base fluid are not consistent and highly dependent on crude oil sources. Thus, there is an impetus towards developing synthetic and environmentally friendly lubricants that are produced from renewable agricultural sources. Esters can be tailored to cater to the ever increasing lubricating challenges and applications without compromising on biodegradability and performance. Synthetic biolubricant esters are usually produced by transesterification or esterification and conventionally synthesized using homogenous catalysts like sulphuric acid, sodium hydroxide/alkoxide or using solid catalysts like Amberlyst-15 and immobilized lipase enzymes. However, these routes are associated with acidic waste water, neutralized salts, soaps or deactivated catalysts. These cause disposal problems and also reduce product purity. In addition, they may catalyze other reactions like etherification or disproportionation.

In reactions involving sub/supercritical alcohols, the necessity of adding a catalyst or a solvent may be obviated. The consequent simplicity of the downstream operations makes the non-catalytic process more economic and environmental friendly (due to reduction in process wastes). Supercritical fluids have attractive properties such as liquid like densities, gas like diffusivities, negligible surface tension, lower viscosities and high compressibilities. Despite many advantages, certain shortcomings exist, such as harshness of operating conditions and requirement of high molar excess of reactants that affect process economics and safety. Most of the studies using supercritical alcohols are focused on the production of fatty acid methyl or ethyl esters that are useful as biodiesel.

However, dicarboxylic acid esters and fatty acid esters of higher alcohols that are useful as biolubricants were not investigated. In this regard, non-catalytic esterification of lauric and stearic acid with supercritical 1-butanol and isoamyl alcohol and the esterification of sebacic acid with methanol and 2-ethyl-1-hexanol were investigated in this research for the first time. The effect of initial molar ratio, temperature, pressure and reaction time on the conversion or yield of esters was investigated. The temperature range investigated for esterification was in between 523 K and 673 K; initial molar ratio was varied up to 40:1 and reaction time up to 90 min. It was observed that with lowering molar ratio, the conversion or yield increases. This was in contrary to triglyceride-methanol/ethanol reacting systems. This is because of the increase in carboxylic acid catalytic activity at lower molar ratios. Higher conversions at lower molar ratios have both economic and environmental advantages. Increase in temperature increases conversion/yield with reaction time. At temperatures 623 K and 673 K degradation was observed at longer reaction times due

to the onset of pyrolytic regime. In case of esterification of sebacic acid with methanol, the monoester concentrations were substantial unlike those with 2-ethyl-1-hexanol where the yield on monoester was below 3 %. Thus in case of reactions with methanol, the molar selectivity (i.e. ratio of moles of diester to monoester) was also evaluated. High yields of dimethyl sebacate up to 87 % and bis (2-ethylhexyl) sebacate up to 83 % with selectivities up to 16 were obtained.

The experimental yield/conversion data was fitted using suitable kinetic models, pseudo first order model for fatty acid esterification, reaction in series model for sebacic acid-methanol reactions and second order reversible model for sebacic acid- 2-ethyl-1-hexanol reactions. In addition, the effect of acid catalytic activity was incorporated in second order reversible model to represent experimental data at lower molar ratios. The rate constants of these reactions were evaluated at different temperatures and activation energies were determined from Arrhenius's plot. The rate constants were also shown to be dependent on the density of the supercritical alcohol at higher molar ratios and to the global densities at lower molar ratios. In case of sebacic acid- methanol reactions, the selectivities vary with both temperature (and thus density) and time. Also, the optimum time at which maximum monoester varies with temperature (and thus densities of the reaction mixture). Further, the critical point of the reaction mixture was determined by Lorentz-Berthelot (LB) mixing rules at different molar ratios. The phase of the reaction can be different from that of pure alcohol at a particular temperature and pressure and can be known by estimating the critical point of the mixture. The phase of the reaction was also shown to vary with progress of the reaction, especially for systems in which the product esters have very different critical point than the parent carboxylic acids

The reaction mixtures obtained can be purified and processed using supercritical carbon dioxide (as a greener alternative) to yield pure esters, in lieu of non-renewable solvents. To design such downstream operations the solubility of these liquid solutes in supercritical carbon dioxide is crucial. In this context, the solubilities of butyl esters, butyl laurate and butyl stearate and sebacate esters, dimethyl sebacate and bis (2-ethylhexyl) sebacate in carbon dioxide were experimentally determined in the temperature range 308 K – 328 K and pressures from 10 MPa - 18 MPa. The solubilities were measured using dynamic technique by flow saturation apparatus. The range of solubilities was in the range of 10^{-4} to 10^{-2} mol mol⁻¹. The solubilities of these esters were compared with those of parent carboxylic acids and other homologous esters.

The solubility of carbon dioxide in the liquid solute can be substantial unlike solid solutes, where it is close to zero. Thus, the compositions of both the phases were correlated to the operating conditions like temperature and pressure. There are no semi-empirical expressions for correlating solubility of liquid solutes in supercritical carbon dioxide, apart from Mendez Teja (MT), Chrastil and Chrastil modified models. A new three parameter semi-empirical expression was developed using a combination of Solution theory and Wilson activity coefficient model (a local composition model) with temperature, T and ratio of density of supercritical carbon dioxide and density of liquid solute, Φ . The new expression correlated the data of the esters investigated in the study within an average deviation within 15 %. The expression was also used to correlate the solubilities of other low-volatile liquid esters useful in lipid processing and reactions. The average deviation was lower than other three parameter models like Chrastil and MT model. The solubility of the supercritical carbon dioxide in the

liquid solute was modeled by using a simple three parameter semi empirical expression based on modified Henry's law. The expression correlates the liquid phase composition of carbon dioxide + liquid solute systems in a wide range of temperatures and pressures. The applicability of this model is wide, encompassing smaller molecular weight like lower alkanes to higher molecular weight fatty acid esters and ionic liquids. The possibility of using this equation in verifying the self consistency of the liquid phase composition data at different temperatures (in parallel with the MT model) was discussed.

Chapter 1 gives a brief review of conventional esterification reactions and the solubility of different low volatile liquid solutes in the context of producing biolubricant esters. Chapter 2 discusses the esterification of fatty acids, lauric and stearic acid with sub/supercritical 1-butanol and isoamyl-alcohol. Chapter 3 deals with esterification of sebacic acid with methanol and 2-ethylhexanol under sub/supercritical conditions to produce diesters. Chapter 4 reports the experimental solubility data of four esters, butyl laurate, butyl stearate, dimethyl sebacate and bis (2-ethylhexyl) sebacate in supercritical carbon dioxide. Chapter 5 and Chapter 6 are devoted to the development of new simple three parameter equations to correlate the supercritical phase and liquid phase compositions respectively, with operating temperature, pressure and density for different liquid solute- carbon dioxide systems. Chapter 7 discusses important conclusions of the research work and also provides a scope for future work.

The esterification reactions reported here were investigated for the first time using supercritical alcohols. Higher conversions were obtained at lower molar ratios and at pressures even half the critical pressure of the alcohol. This research opens up

new vistas for synthesis of biolubricant esters in supercritical fluids obviating the need to add an external catalyst. Further, new experimental solubility data for four biolubricant esters were reported, that would be useful in designing green separation techniques using supercritical carbon dioxide. In addition, two new simple three parameter semi-empirical models were developed in this study that could correlate both the supercritical and liquid phase compositions with respect to pressure, temperature and density of the supercritical fluid.