Chapter 1

Introduction and Literature Review:
Chemical modifications of lipids for applications in chemical industry

The chemical process industries, all over the world, have been facing the challenges of developing innovative processes and products in the wake of highly globalized trade competition and stringent environmental regulations\(^1\). The term Green Chemistry has been coined to promote the movement towards more environmentally acceptable and sustainable chemical processes and products. The ‘Twelve Principles of Green Chemistry’, which were formulated in the 1990s, provide guidelines for chemists to develop clean, environmentally benign methodologies that are sustainable for the long term and that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products\(^2\).

According to the seventh principle of Green Chemistry, a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. The term ‘Renewable Resources’ primarily includes carbohydrates (starch, cellulose, sugars) and lipids (animal and vegetable fats and oils, phospholipids etc.). Carbohydrates are the most abundant organic compounds (around 75-80% of biomass) on the planet. They constitute a suitable replacement for fossil fuels since they contain a considerable amount of carbon and hydrogen. Utilization of natural products such as plant oils and natural fats has attracted great attention in both scientific and industrial areas in recent years. They can be used and are being used to produce valuable chemical feedstocks and macrocyclic frameworks for natural product synthesis. The wide range of renewable raw materials with varying properties and differing chemical compositions are available at the annual production rate of approximately 170 billion tons\(^3\). Around 6 billion t/a (3.5%) are utilized in the form of timber, grain and other foodstuffs. The rapid depletion of crude oil reserves, escalating fuel prices and the concern over climate change catapulted into global interest for utilizing the remaining 96% (quantitatively in the order of the total reserve of mineral oil) crop-based feedstocks as renewable alternatives to petroleum-based feedstocks for energy generation and the synthesis of new platform chemicals\(^4\)\(^-\)\(^6\). Bio-based chemicals typically are cheap, readily available, low in toxicity, \(\text{CO}_2\) sequestering, biodegradable and eco-friendly, making them prime candidates for an alignment of industry to the principles of green chemistry and sustainability. In spite of this fact, the applications that use biomass as starting materials are currently limited to
only 10-12% of the overall organic chemical industry and include adhesives, textile and leather chemicals, surfactants, cleaning agents, perfumes and flavours, cosmetics, coatings/ paints, printing inks, crop protection, lubricants/ greases and dietary supplements. Chemists have much to contribute to meet this challenge and the future of green chemistry will depend on innovations that consolidate and integrate the Twelve Principles as a framework for intentional design of routes for utilisation of renewable materials. The detailed study of the chemistry of these renewable materials and the exploration of their chemical derivatizations with due stress on techno-commercial feasibility analysis, which is the objective of present investigations, is absolutely necessary on the way to sustainable and economical usage of biomass as renewable feedstock for organic chemical industries.

1.1 A. Vegetable oils and fats as feedstock for chemical industries, their world production and economics

Lipids are water insoluble organic biomolecules that can be extracted from cells and tissues by nonpolar organic solvents such as hexane, acetone, ether, chloroform etc. and are widely distributed in nature. Lipids can be further classified as simple lipids (fats, waxes), conjugated lipids (phospholipids, lipoproteins, glycolipids) and derived lipids (terpenes, steroids, fat soluble vitamins [A, D, E, K], carotene, tocopherols, squalene). The diverse utility as foods, fuels, lubricants and starting materials for other chemicals result from the unique chemical structures and physical properties of lipids. Vegetable oils are the most important renewable and readily available part of a large family of lipids.

The oils and fats of commerce are predominantly made up of triesters of glycerol with fatty acids (FA) called triacylglycerol or triglycerides (Fig. 1.1). FA are almost entirely straight chain aliphatic saturated, monounsaturated or polyunsaturated carboxylic acids. The broadest definition includes all chain lengths, but most natural FA are C_4 to C_22, with C_{18} most common. The principal raw materials from which the natural fatty acids are derived are tallow, crude tall oil, coconut, palm kernel, sunflower, castor and soybean oils. Crude oils or triglycerides, when first extracted (generally >95%), are accompanied by diglycerides, monoglycerides and free FA, but they may also contain phospholipids, free sterols and sterol esters, tocols (tocopherols and tocotrienols), triterpene alcohols, hydrocarbons and fat-soluble vitamins. During refining, some of the minor components are removed, wholly or in part, and useful materials may be recovered. For example, phospholipids are separated during degumming, and deodoriser distillates contain fatty acids, along with valuable sterols, sterol esters, tocols, etc.
The world’s production and consumption of natural oils and fats has grown from 79.2 million metric tones\(^7\) (MMT) in 1990 to 117 MMT in 2001. The annual global production of the major vegetable oils amounted in 2007/08 to 128 MMT, increasing in 2008/09 to 132 MMT, and in 2009/10 137 MMT are expected\(^8\). In addition, about 31 MMT of minor plant oils and animal fats were produced and consumed\(^9\). It is expected that the average annual world oil production will increase in the years 2016 to 2020 to 184.7 MMT\(^{10}\). Sunflower seed oil is obtained from *Helianthus annuus* grown mainly in Russia and Ukraine, Argentina, Western and Eastern Europe, China and the United States\(^{11}\). World production of sunflower oil is around 9 MMT, amounting to 8% of the total vegetable oil production\(^{12}\). The projected production for 2008–2012, according to the literature\(^{10,13}\), would be 12 MMT. Soybeans (*Glycine max*) are grown mainly in the United States, Brazil, Argentina and China\(^{11}\). At almost 30 MMT per annum\(^{14}\) (2006-10 forecast 33.6 MMT)\(^{10}\), soybean oil is produced in greater amounts than any other oil. Grown mainly in Indonesia and the Philippines, the annual production of coconut oil [coconut palm (*Cocos nucifera*)] exceeds 3 MMT\(^{11,14}\). Castor oil (*Ricinus communis*) is produced mainly in India, Brazil and China at a world production level of 0.4-0.5 MMT\(^{11,14}\). India is the world’s largest exporter of castor oil. Groundnut oil, obtained from the legume Arachis hypogea, is also known as peanut oil, monkeynut oil or arachis oil. The plant is grown widely, especially in India, China and the United States. Many of the nuts are consumed as snacks, but crushing still yields about 5.5 MMT of oil each year\(^{11,14}\). In general, Malaysia, Indonesia, and Argentina are prominent excess-supply producers of oils and fats while India, the European Union countries, and China are notable high-demand areas that supplement regional production through imports. In India, in the Oil Year 2007-08 (Nov. 2007- Oct. 2008), the net availability of edible oils from all domestic sources was 8.654 MMT while the consumption of Edible Oils was 14,262 MMT (source: Net availability and consumption of edible oils: Directorate of Vanaspati, Vegetable Oils & Fats, India). Thus the surplus requirement was met mainly through imports. Despite overall increases
in production of oils and fats, changes vary from year to year and individual oils may even show a decline in particular years. The uneven changes from year to year result in variations in the relation between supply and demand and consequently affect the stock status. When stocks rise, prices fall, demand increases and production declines because it becomes less profitable. On the other hand, when stocks fall, prices rise, demand is stifled, but production then increases as profit margins grow. In this way the market takes care of changes in agricultural production arising both from man-made decisions and from changes in climate.

Oils and fats differ in composition of the alkyl chains depending on their origin. Table 1.1 presents the FA composition of some commercially important vegetable oils. Oils rich in saturated FA have poor low-temperature flow properties, and those rich in polyunsaturated FA are of low oxidative resistance. Vegetable oils rich in monounsaturated FA have optimum oxidative stability and low-temperature properties15. The edible uses of vegetable oils include the preparation of shortening/bakery fat, vanaspati, margarines, and mayonnaise, besides routine use as cooking and frying oil and as salad oil. In addition to food uses, the long-chain unsaturated FA vegetable oils such as soybean, sunflower, and rapeseed have found their way into the plastics, pharmaceutical products, inks, adhesives, coatings and many other industries. For example, the use of soybean oil in lubricants15, oleochemicals16, and bioplastics17 is reported. Vegetable oil-based inks, which cost even less than the petroleum oil-based inks, have been formulated for various specialized applications. Containing around 70% linoleic acid, the traditional sunflower oil is semidrying oil and can be used, like soybean oil, in the manufacture of resins for paint and press-ink formulations18.

Mineral-based lubricants lead the lubricant market. However, with the advancement of the need for biodegradable products, vegetable oils have become popular, because they are also better lubricants. Vegetable oils with high oleic (C18:1) content are considered to be the potential environmentally friendly base fluids to substitute conventional mineral oil-based lubricating oils, synthetic fuels (biodiesel, biogasoline) and synthetic ester19-21. In view of the higher oxidative stability of high-oleic sunflower oil, it is used as diesel and gasoline engine lubricant. The groundnut oil produced is virtually all used within the countries of production for edible purposes. Coconut oil, the medium chain saturated FA oil (mainly lauric C12 and myristic C14 FA), normally commands a higher cost over other vegetable oils. It is an important source for the production of emulsifiers, detergents, cosmetics etc. In toilet soap, high lauric content provides the quick
lathering properties. Castor oil differs from all other commercial oils in being rich in ricinoleic acid (~90%, 12-hydroxyoleic). This hydroxy acid has several interesting properties and is converted to a range of useful products to substitute those obtained from petroleum such as lubricant, surface coating, nylon, perfumery chemicals and organic intermediates for several industries. Long chain saturated FA (mainly stearic C\text{18} and palmitic C\text{16}) oils such as palm oil, sal fat, mahuwa fat have relatively high oxidation stability and provide the hard fat components of soaps.

1.1 B. Primary and secondary oleochemicals

The direct use of fatty oils for industrial purposes is limited to relatively small applications. The chemistry and technology of oils and fats derived industrial products i.e. oleochemicals run parallel to those of petrochemicals. Majority of the oleochemicals, being derived from oils and fats, are straight long chain, even numbered, primary functional compounds and their advantages including biodegradability and negligible sulfur, nitrogen and heavy metal content can be illustrated by several of the principles of green chemistry\textsuperscript{22,24}.

Oleochemicals derived from splitting (hydrolysis) or transesterification of natural fats and oils such as fatty acids (FA), mono-alkyl (mostly methyl) fatty esters (biodiesel-substitute for diesel fuel), and glycerol, are termed as basic oleochemicals. Further processing of these basic oleochemicals and their various fractions by different unit processes/chemical modifications, such as transesterification and esterification (e.g. sucrose polyesters, monoglycerides), saponification and coprecipitation (metallic soaps) hydrogenation and hydrogenolysis (e.g. fatty alcohols), ethoxylation (e.g. alcohol ethers), sulphonation and sulphation (e.g. ester sulphonates, turkey red oil), ammonolysis and amidation (nitrogen derivatives), ozonolysis (azealic/ pelargonic acids), epoxidation and hydroxylation, dimerization and polymerisation, pyrolysis, alkali fusion (Fig. 1.2), produce secondary oleochemical or specialty chemical products for utilisation as surfactants, emulsifiers, lubricants, plasticizers, additives, bactericides, fungicides, etc. Sunflower oil, either traditional or high oleic, may be used in bio-carburant in the form of methyl esters. The use of vegetable oils as a substitute for petroleum-based diesel has been replaced by the use of their methyl or ethyl esters as biodiesel. The importance of biodiesel as a partial or total substitute for petroleum-based fuels has increased in the last two decades. The fatty acid methyl esters (FAME) of soyabean oil are blended with diesel fuel at a ratio of 20:80 for use in ignition engines\textsuperscript{25}. The caproic to capric (C\text{6}–C\text{10}) fatty acid fractions, comprising approximately 15% in coconut oil, are good materials for...
plasticizer range alcohol and for polyol esters. The latter are used in high-performance oil for jet engines and for the new generation of lubricants. These acid fractions are also the basic material for the manufacture of medium-chain triglycerides, a highly valued dietary fat. Glyceryl monoesters and wax esters find application as food emulsifiers, mold release agents, and lubricants for the plastic industry. In a variety of polymer applications, such as coatings, large amount of solvents has to be used. Use of hydrocarbon and chlorinated solvents provide volatile organic emissions with photochemical ozone creation potential. Ester solvents, typically produced from FA and/or fatty alcohols, represent the largest group of green solvents\textsuperscript{26}. The production of FAME of soyabean oil as environmentally friendly solvent is reported\textsuperscript{27,28}.

The main non-food use of oleochemicals is in the production of surfactants. The amphiphilic properties of fatty acids, exploited for centuries in the use of soaps, can be modified by changing the carboxyl group into other hydrophilic groupings, giving anionic, cationic, amphoteric and nonionic surfactants. Soap is one of the oldest known oleochemical surfactant manufactured from saponification of oils. Fatty amines, produced by the reaction of fatty acids with ammonia and hydrogen, are the most important nitrogen derivatives of fatty acids. Polyglycol ethers, produced by the reaction of fatty alcohol with ethylene oxide, constitute the most important class of nonionic surfactants. Monoalkyl phosphate, fatty alcohol ether phosphate, and fatty alcohol sulfo succinate are some of the specialty surfactants derived from fatty alcohol with specific applications in the cosmetics and other chemical industries. Alkanolamides, formed by the reaction of fatty acids or esters with monoethanolamine or diethanolamine are popularly used as foam boosters for shampoos and detergent products.

Parallel to the growth of the petrochemical industry, the fats and oils industry has grown, and the oleochemistry has become an important area of research and technology in several institutions and industries over the years. For long it has been considered that oil and fat consumption was shared between food, feed, and industrial use in the ratio 80:6:14, but with increasing production of biodiesel this is probably now closer to 74:6:20\textsuperscript{29}. Many new FA plants, with a cumulative capacity of 1.5 MMT have been built in Southeast Asia\textsuperscript{30} (coconut and palm oil producing region). Consumption of fatty acids in the United States, Western Europe, and Japan totaled 2.5 MMT in 2001. There was a sharp decline in production and consumption of fatty acid in North America after the events of September 2001. However, growth is expected at the rate of 2.3% for the consumption of split acids for the period 2000–2006. Growth in Western Europe is expected at the rate of 1.2%/yr for
Table 1.1 Fatty acid composition of major vegetable oils

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of the Oil</th>
<th>ρ</th>
<th>S. V.</th>
<th>I. V.</th>
<th>% Fatty Acid Composition</th>
<th>Any special fatty acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Castor</td>
<td>0.945-0.965/25°C</td>
<td>177-187</td>
<td>83-86</td>
<td>C14: 2.0, C16: 1.0, C18: 7.0, C18:1: 5.0</td>
<td>----</td>
</tr>
<tr>
<td>2</td>
<td>Coconut</td>
<td>0.917-0.919/25°C</td>
<td>251-263</td>
<td>7.5-10.5</td>
<td>13.0-19.0, 8.0-11.0, 1.0-3.0, 5.0-8.0, 0-1.0</td>
<td>----</td>
</tr>
<tr>
<td>3</td>
<td>Groundnut</td>
<td>0.910-0.915/25°C</td>
<td>188-195</td>
<td>84-100</td>
<td>6.0-9.0, 3.0-6.0, 52.0-60.0, 13.0-27.0</td>
<td>----</td>
</tr>
<tr>
<td>4</td>
<td>Mustard</td>
<td>0.906-0.910/25°C</td>
<td>169-176</td>
<td>98-110</td>
<td>1.5, 0.4, 22.0, 14.2</td>
<td>6.8</td>
</tr>
<tr>
<td>5</td>
<td>Soyabean</td>
<td>0.916-0.922/25°C</td>
<td>189-195</td>
<td>128-143</td>
<td>tr.0.5, 7.0-11.0, 2.0-6.0, 22.0-34.0, 43.0-56.0</td>
<td>5.0-11.0</td>
</tr>
<tr>
<td>6</td>
<td>Sunflower</td>
<td>0.915-0.919/25°C</td>
<td>188-194</td>
<td>125-140</td>
<td>3.0-6.0, 1.0-3.0, 14.0-35.0, 44.0-75.0</td>
<td>0.6-4.0</td>
</tr>
<tr>
<td>7</td>
<td>Cottonseed</td>
<td>0.915-0.926/15°C</td>
<td>191-196</td>
<td>103-115</td>
<td>0.4, 20.0, 2.0, 35.0, 42</td>
<td>----</td>
</tr>
<tr>
<td>8</td>
<td>Palm</td>
<td>0.921-0.925/15°C</td>
<td>196-205</td>
<td>48-58</td>
<td>0.5-2.0, 32.0-45.0, 2.0-7.0, 38.0-52.0, 5.0-11.0</td>
<td>----</td>
</tr>
<tr>
<td>9</td>
<td>Linseed</td>
<td>0.931-0.938/15°C</td>
<td>189-196</td>
<td>170-180</td>
<td>4.0-7.0, 2.0-5.0, 12.0-34.0, 17.0-24.0, 35.0-60.0</td>
<td>0.3-1.0</td>
</tr>
</tbody>
</table>

ρ: specific gravity; I. V.: Iodine value; S. V.: Saponification value; H. V.: Hydroxyl value; C6: Caproic acid; C8: Caprylic acid; C10: Capric acid; C12: Lauric acid; C14: Myristic acid; C16: Palmitic acid; C18: Stearic acid; C18:1: Oleic acid; C18:2: Linoleic acid; C18:3: Linolenic acid; C20: Arachidic acid.
the period 2001–2006. Japan’s consumption is expected to decline$^{30}$. Recent data for the Philippines listed a capacity of 25,000 t of alcohol products from coconut oil by the fatty acid hydrogenation process for Cocochem and 4,000 t for Colgate. Philippines’ Kao produced 30,000 t of alcohol products from coconut oil using the methyl ester hydrogenation process$^{31}$. In 2008, biodiesel production and capacity amounted globally to 11.1 and 32.6 MMT, respectively$^{32}$. This is most remarkable because biodiesel as fatty acid methyl ester can also be used as chemical feedstock. Moreover, genetic engineering offers a new way of optimizing the properties of oleochemicals by controlling the FA distribution. This allows us to change the composition of plant oils to control the structures that produce oleochemicals with better properties. Thus the oleochemical industry is fairly well developed and its future share of chemical industries, which currently stands at 10%, may go up because of a reliable supply of raw materials.

1.1 C. Chemical modifications of vegetable oils for synthesis of oleochemicals

The physical and chemical properties of oils and fats can be modified through the use of diverse derivatization pathways as shown in Fig. 1.2. In fact, chemical modifications of vegetable oils constitute an important route to develop new efficient and environmentally friendly reaction pathways leading to new products or to find new applications for already existing oleochemicals$^{33}$. This strategy can contribute to decrease our dependence on non-renewable, and therefore limited, natural resources such as mineral oil. For example, a high degree of multiple C=C unsaturations in the fatty acid (FA) chain (mainly linoleic C$_{18:2}$ and linolenic C$_{18:3}$ FA) of many vegetable oils (e.g. soybean/ linseed/ sunflower/ safflower etc.) causes poor thermal and oxidative stability and confines their use as lubricants to a modest range of temperature. The bis allylic protons in FA chain are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds, which ultimately results in insoluble deposit formation and an increase in oil acidity and viscosity$^{34}$. Vegetable oils also show poor corrosion protection and the presence of ester functionality renders these oils susceptible to hydrolytic breakdown. Although use of additives$^{35}$ (antioxidants and pour point depressants) can overcome these shortcomings to some extent, the major way to improve these properties of vegetable oils is chemical modifications of fatty acid chains of triglycerides at the sites of double bonds and carboxyl groups.

Thus the chemical modifications through application of various unit processes, as shown in Fig. 1.2, are essential for obtaining oleochemicals with multifunctionality, improved oxidative, thermal and photostability and good low temperature properties for explorations in chemical industries$^{36,37}$. 
Fig. 1.2 Oleochemicals derivatization pathways
The exact FA composition of various plant oils (Table 1.1) gives indications of the most likely transformations and the probable characteristics of the oleochemicals formed after chemical modifications, which are required to improve the physicochemical and performance characteristics of these derivatives. The main compositional difference is the chain-length distribution of the fatty acids associated with the fats or oils. The chain length of the feed stock, C_{12}-C_{14} from lauric oils, C_{22} from high erucic rape and fish oils, and C_{16}-C_{18} from most other sources, can be used to modify solubility, hydrophobicity and other characteristics. The chemical modification of triglycerides is performed using the reactivity of the functional groups in their structure. In respect of chemical modifications, oils and fats carry following active chemical sites that can be used for derivatisation, functionalisation or polymerization:

i) The terminal functional group mostly ester or carboxyl group- Traditionally, industrial oleochemistry has concentrated predominantly on exploiting synthetic methods- esterifications\(^{38}\), transesterifications\(^{39}\), hydrogenolysis, saponifications, acylation\(^{40}\) etc. applied to the carboxylic group of FA to synthesize major industrial oleochemicals.

ii) Single or multiple double bonds- Chemical modification of seed oils at the unsaturated bond sites results in changes to the physical properties of the substrate and allows products to be tailored to meet specific applications. Currently less than 10% of the modifications have involved the hydrocarbon backbone of the fatty acid\(^{41,42}\).

iii) Carbon atom \(\alpha\) to the functional group- although the most reactive sites in fatty acids are the carboxyl group and double bonds, methylenes adjacent to them are activated, increasing their reactivity. Only rarely do saturated chains show reactivity.

iv) Secondary OH group- The presence of hydroxyl group on castor oil makes it vital industrial raw material.

v) Other special functional groups- e.g. epoxy group in Vernolic acid present in oil obtained from *Euphorbia lagascae*.

Carboxyl groups and unsaturated centers usually react independently, but when in close proximity, both may react through neighboring group participation. The industrial exploitation of oils and fats, both for food and oleochemical products, is based on chemical modification of one of these five active sites. The continued development of oleochemistry opens up for several reaction routes involving selective transformation of the alkyl chain, for example sulfonation, with the potential of producing new highly-branched and charged hydrophobes from abundant natural material\(^{43}\). The transformations by reactions of the
carbon-carbon double bonds in the fatty acids such as epoxidation and epoxy ring-opening\textsuperscript{20} hydrogenation\textsuperscript{44}, hydroformylation, hydrocarboxylation, ozonolysis, estolides formation\textsuperscript{45}, metathesis\textsuperscript{46} and dimerization, are becoming increasingly important industrially for the improvement in the oxidative stability and attaining the optimal characteristics for extreme applications\textsuperscript{47}. There is also scope for functionalizing the aliphatic chain, but this has not been widely used commercially. Introducing functionality to the alkyl chain through radical, electrophilic, nucleophilic, pericyclic, and transition metal catalyzed addition to carbon-carbon double bonds leads to novel compounds with commercial potential. The chemical transformation of triglycerides affords a wide variety of monomers for the synthesis of linear\textsuperscript{45}, hyper-branched\textsuperscript{48} or cross-linked structures\textsuperscript{49}.

Subsequent sections present literature review on chemical modifications undertaken in present investigations.

1.2 Sucrose esters

Although scientists have reported numerous ways of making surfactant linkages (amphiphilic) for a large number of different carbohydrates used, it is clear from an industrial perspective that only a few carbohydrates such as sucrose fulfil the criteria of price, quality, and availability to be an interesting raw material source. Sucrose (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}) is one of the most abundant, renewable and inexpensive international agricultural carbohydrate products in the world, found in sugar cane, sugar beet and many other plants. It is produced at a very high scale of production volume of 130 MMT per annum [The figure, estimated by Cerestar, Henkel, is based on the crop cycle of 2002-03]. According to the revised estimate of ISMA (Indian Sugar Mill Association), the annual production of sugar in 2012 at the end of sugarcane season would be 24.3 MMT. The data indicates the abundant availability of sugar as raw material for chemical industries. Chemical transformations of sucrose are much developed in the fermentation domain, in order to produce alcohol, yeast, organic acids, etc. Another strategy (sucrochemistry) is to keep the disaccharidic structure with the goal of taking advantage of its physical properties (polarity, hydrophilicity, biodegradability, higher compatibility with biological systems, low toxicity, skin-compatibility etc.) and bringing them into a new molecule. In this respect, the targets are nonionic surfactants, eco-friendly detergents, associative polymers, rheology modifiers, sweeteners, body builder, fat substitutes, non digestible oligosaccharides etc\textsuperscript{50-52}.

Sucrose monoester (SE) is a green surfactant while sucrose polyester (SPE) is a low calorie fat substitute, both being derived by transesterifying sucrose with edible oil/ fatty acids or esters either by chemical or enzymatic processes. Development of the technique for
synthesis of sucrose esters was one of the first major achievements of the Sugar Research Foundation⁵³.

1.2.1 Synthesis and characterization of sucrose esters

Considering the amphiphilic structure of a typical surfactant with a hydrophilic head group and a hydrophobic tail, it has always been a challenge to attach a sucrose molecule as the perfect hydrophilic group, due to the numerous (eight) hydroxyl groups, to a fat and oil derivative such as fatty acid/ester/alcohol⁵⁴. Sucrose is a disaccharide of α-glucose and fructose. These two moieties are connected at their anomeric carbon atoms. It does not contain a hemi-acetal linkage and so, it is a nonreducing sugar. Its chemistry is then limited to its eight hydroxyl groups, of which three are primary (C₁, C₆⁻, and C₆) and five are secondary, which compete during the derivatization step with methyl esters of fatty acids derived from edible fats and oils including hydrogenated fats and oils such as stearic acid, palmitic acid, erucic acid and other fatty acids. The primary site for transesterification appears to be the 6th position of the glucose portion of the molecule⁵⁵. The base catalyzed transesterification reaction proceeds faster than its acid catalyzed counterpart⁵⁶.

Typically, the sucrose esters are prepared through the base catalyzed transesterification of sucrose with vegetable oils/fatty acid methyl esters, using sodium methoxide or potassium carbonate or alkali metal soaps as a catalyst and in the presence of suitable basic solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), isobutanol, or methyl ethyl ketone⁵⁷,⁵⁸ (Fig. 1.3). Methanol is released as a by-product through this reaction. Its removal by distillation during synthesis (semi-batch process) drives the equilibrium in favor of the sucrose ester and improves the yield of the desired product. Lithium soap, as catalyst, will shorten ester exchange time 2-3 hr relative to other method and the yield of production is high. In general, mixed alkali metal soap (lithium oleate and sodium oleate) with proper ratio as catalyst can improve the yield of sucrose ester⁵⁹. A complex product mixture consisting of mono-, di-, tri, tetra-, and pentaesters is formed. The reaction is stopped by the addition of lactic acid to neutralize the reaction mixture. Through the choice of sucrose to fatty acid mole ratio, reaction time, speed of methanol removal, the ratio of mo-, di-, and polyester can be influenced. It is difficult to obtain pure monoesters by this route because they disproportionate to sucrose and diesters. Hence diester predominates at lower reactant ratios⁶⁰ (2:1). Co-proportionation of diesters with sucrose resulted in monoesters which still contained 10% diester. By varying the degree of esterification of the sucrose molecule it is possible to obtain emulsifiers with HLB values ranging from 1 up to 16
for the high SE content. SPE products (higher degree of substitution) are very hydrophobic and of limited application potential.

![Chemical Structure](image)

Fig. 1.3 Synthesis of sucrose esters by base catalysed (K₂CO₃) transesterification with FAME.

The conventional base-catalyzed high temperature production of sucrose esters has a low selectivity, forming coloured derivatives as side products⁶¹,⁶². Several methods have been developed to achieve higher selectivity in the reaction or provide economical purification procedures and, as a result, a high quantity of hydrophilic monoester or hydrophobic polyester. Increase in the monoester content was achieved in a sucrose laurate product by alcoholysis with methanol⁶³. An alternate improved one-step process involves dissolving sucrose ester in propylene glycol and emulsifying methyl esters into this solution followed by thin film reactive distillation. The glycol is distilled off and in the distillation process, transesterification takes place. It permits greater yields of the polyesters at 110-145⁰C within 5 hrs, eliminating use of toxic solvents and more efficient removal of byproducts⁶⁴,⁶⁵. Procter & Gamble holds two patents on synthesis of SPE⁶⁶,⁶⁷ during 2005-06. The direct esterification of sucrose with fatty acid chlorides⁶⁸ is reported. Powdered white granulated sugar and methyl carbityl palmitate were reacted using different metal soaps as catalyst at 185⁰C⁵⁹. The base-catalyzed synthesis of four sucrose fatty acid esters (caprylate, laurate, myristate, and palmitate) was performed in DMSO by transesterification of sucrose with the corresponding vinyl esters using disodium hydrogen phosphate as catalyst. In using a molar ratio sucrose/vinyl ester 4:1 and mild reaction conditions (40⁰C and atmospheric pressure), yields were higher than 85%. The isolated sucroesters had a higher percentage of monoesters (around 90%) and a lower content of diesters in comparison with commercial derivatives. In all cases, 2-O-acylsucrose was the major product (around 60%) in the monoester fraction. For example, 72% yield of 2-O-lauroyl sucrose was obtained at 40⁰C for 5 hrs with vinyl laurate as acyl donor⁶⁹. The author holds patent for this improved procedure⁷⁰. A highly regioselective
conversion of sucrose into 6-O-acyl derivatives is reported. First sucrose was transformed into the dibutyltin acetal, thus enhancing the nucleophilicity at the C_6 oxygen and restricting the subsequent acylation reaction\(^{71}\). The enzyme-catalyzed synthesis of sugar esters provides regio- and stereo selective products\(^{72-74}\). Enzymatic sugar ester syntheses catalyzed by an immobilized lipase were investigated, including the solubility, water content, molar ratio of sugar/acyl donor, and enzyme stability\(^{75}\). Enzymatic synthesis of fatty acid esters of di- and tri-saccharides is limited by the fact that most biological catalysts are inactivated by the polar solvents (e.g. DMSO, DMF) where these carbohydrates are soluble. To overcome this limitation, the uses of mixtures of miscible solvents (e.g. DMSO and 2-methyl-2-butanol) were proposed as a general strategy to acylate enzymatically hydrophilic substrates.

However, most of the above methods remain limited to laboratory scale because of the process economics. Standard technology (conventional method, \textbf{Fig. 1.3}) for production of SE/ SPE is still the transesterification combined with a series of purification steps to remove impurities and residual solvents. The purification procedures include the use of solvents, special extraction and crystallization techniques, and equilibrium reactions. The sugar was precipitated from the reaction mixture by adding toluene, xylene, butanol or isobutanol as a solvent. The solvent permits separation into a plurality of layers containing sucrose esters of different degrees of substitution, which are recovered from the separate layers. Mixing with water and freeze-drying the aqueous mixture may further refine the separate layers. Reaction and extraction solvents and methanol are removed by the distillative concentration/ purification processes. Vacuum may be applied to accomplish the distillation at lower temperature. As a consequence of the manufacturing process, several trace impurities may be found in the final purified products. An optimized solvent-free process using water for removal of impurities and spray process for drying of product has been described\(^{76}\). Transesterification of sucrose in excess FAME (without additional solvent) at about 140\(^\circ\)C (around 20 hrs) and simultaneous removal of methanol to form sucrose esters with a high degree of esterification (DE= 4), subsequent alcoholsysis of the sucrose ester by addition of methanol at 75\(^\circ\)C in two steps (step 1 transesterification: 45 min, step 2 transesterification: 75 min) to form sucrose monoester and FAME, and removal of residual methanol and FAME using a thin-film evaporator (160\(^\circ\)C, 0.2–0.3 mbar)\(^{63}\) permit high yield of sucrose monoesters. Product analysis by high-performance liquid chromatography shows the increase of the sucrose monoester (SE) content to 48% (DE= 1.8, reaction A) and 57% (DE= 1.6, reaction B) relative to sucrose diester and sucrose oligoesters (SPE). The Japanese
firm of Dai-Nippon has utilized large excess of sucrose and K$_2$CO$_3$ as a catalyst, for manufacture at 90°C under vacuum. Today, the major producers of sucrose esters are Dia-Ichi Kogyo Seiyaku and Mitsubishi in Japan, Croda in the United States, Sisterna (a joint venture of Dai-Ichi with Suiker Unie from The Netherlands), and Goldschmidt in Germany.

Thin layer chromatography (TLC) has been widely used as a preliminary qualitative technique for the analysis of SE/ SPE to give an impression of the reaction. This technique is considered as a rapid, advantageous and simple method for the preliminary investigation of SE/ SPE synthesis. HPLC is an efficient tool for analyzing and quantifying SE/ SPE in a reaction mixture. This technique is more convenient than gas chromatography as it does not require previous derivatization of the sample. Many procedures for SE/ SPE separation with HPLC were reported with the different eluent systems.

1.2.2 Reaction mechanism and kinetics of synthesis of sucrose esters

The transesterification reaction mechanism of base catalyzed synthesis of sucrose esters is shown in Fig. 1.4 which proceeds by a two stage transesterification process.

\[
\text{Sugar—OH} + \text{Base} \rightleftharpoons \text{Sugar—O}^- + \text{Base—H}^+
\]

Potassium soaps provide a homogeneous melt of sucrose and fatty acid methyl esters. Initially, the base reacts with the alcohol, producing an alkoxide and the protonated catalyst. The alkoxide then attacks the carbonyl group of the fatty acid methyl ester. This nucleophilic attack generates a tetrahedral intermediate. The alkyl ester and the anion of the fatty acid are then formed. The anion deprotonates the catalyst and generates an active species which reacts with a molecule of the alcohol, starting another catalytic cycle.

The rate constants, activation energies, Arrhenius factor and mechanism of inhibition for base catalyzed hydrolysis of sucrose laurate, sucrose sulphenyl laurate and sucrose ethyl laurate were investigated at several temperatures in pH 11 buffer. At 27°C sucrose laurate
hydrolyzed fastest and sucrose ethyl laurate slowest\textsuperscript{79}. A kinetic model for the synthesis of the sucrose esters without solvent is developed. It implies a solid/solid/liquid reaction between sucrose (solid) and methyl palmitate (liquid). The second solid (potassium carbonate) acts as a catalyst. The reaction medium is heterogeneous and pasty. The viscosity increases with the chemical reaction extent. Activation step of sucrose (solid) by potassium carbonate (solid) is taken into account which corresponds to the overcrossing of the interfacial barrier and the contact between the two solids and is associated to the viscosity of the medium. The second important parameter is molar ratio, which takes into account the hydrophobic effect during the formation of diesters\textsuperscript{80}. The literature describes several molecular models of heterogeneous kinetics, for example:

- Park and Levenspiel model\textsuperscript{81}: it represents conversion versus time with S shape curves.
- Hao-Tanaka model\textsuperscript{82}: it describes the reaction between two solids and takes into account the number of contact points between the particles.
- The shrinking core model and the uniform conversion model\textsuperscript{83}.

### 1.2.3 Properties and applications of sucrose esters

Sucrose esters (SE/ SPE) occur as white to yellow-brown powdery or massive substances, or as colourless to red-brown, viscous resinous or liquid substances. Sucrose monolaurate forms clear, low viscous aqueous solutions at 30% strength while those of C\textsubscript{16}-C\textsubscript{18} fatty acids forms gels. SPEs, however, are completely water insoluble. They are stable at pH 4 to 8 and at temperatures up to 180\textdegree{}C. Sucrose monooleate, however, decomposes at 120\textdegree{}C. The physical and chemical properties, including the lipophilic character, of the sucrose esters vary depending on (i) the alkyl chain length of acyl group, (ii) the degree of substitution or number of hydroxyl groups replaced by ester groups in the compound, (iii) the degree of unsaturation of the acyl chain.

i) SE as non-ionic surfactant

Sucrose ester with three or lesser fatty acids is suitable as surfactants and food additives because of their emulsifying, stabilizing, and conditioning properties\textsuperscript{84,85}. The amphiphilic behavior of sucrose based surfactants result from the hydrophilic free hydroxyl groups and hydrophobic alkyl chain. The uses of surfactants are determined by the particular functionality with respect to their solubility in oil and water which can be expressed and quantified as their hydrophilic-lipophilic balance or HLB value. Wide range of HLB values ranging from zero to twenty, are obtained by changing the characteristics of the fatty acid used in their preparation\textsuperscript{86}. Unlike the alkyl ethoxylates, the sucrose esters do not
significantly change their HLB with increasing temperature. Consequently, increasing the temperature does not induce a phase inversion in micro emulsion systems based on sucrose esters, as was observed in micro emulsions based on alkyl ethoxylate\(^87\). The properties of sucrose esters can range from water soluble surfactants (high HLB, most hydrophilic) to oil soluble surfactants (low HLB, most hydrophobic) as shown in **Table 1.2.** HLB values of some pure SE is as given below\(^88\): sucrose monostearate(C\(_{18}\))-11.2, sucrose monopalmitate(C\(_{16}\))-11.8, sucrose monomyristate(C\(_{14}\))-12.4. Thus with decrease in chain length from C\(_{18}\) to C\(_{14}\), the hydrophilicity of SE increases. The softening temperature and surface tension of 1% solution of sucrose monolaurate were 90-91°C and 33.4 dynes/cm, respectively\(^89\). The CMC (mol/lit) of 6-\(O\)-lauroyl sucrose and 6-\(O\)-myristyl sucrose at 30°C were found to be 5.14-5.31 X \(10^{-4}\) and 0.71-0.88 X \(10^{-4}\), respectively. These CMC values are lower than those of ethoxylates\(^71\). Thus SE of fatty acids having 12 or more carbon atoms (at low degree of substitution, preferably monoester) are expected to display surface active properties. Long chain SE have shown promise as surfactant and compare well in foaming, wetting, emulsification and overall detergency performance with other surface-active compounds and for some applications even superior\(^58,90\). They are not sensitive to hard water, and some of the SEs are moderate foaming agents\(^91\). Mixtures of regioisomers, as well as mono-, di- and triesters are used as emulsifiers, whose resulting physicochemical properties depend on the average degree of substitution and fatty acid chain length.

**Table 1.2 Approximation of HLB values of surfactants as a function of their solubility in water**\(^92\)

<table>
<thead>
<tr>
<th>Solubility in water</th>
<th>HLB Values*</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble</td>
<td>4-5</td>
<td>Water in oil emulsifier</td>
</tr>
<tr>
<td>Poorly dispersible</td>
<td>6-9</td>
<td>Wetting agent</td>
</tr>
<tr>
<td>Translucent to clear</td>
<td>10-12</td>
<td>Detergent</td>
</tr>
<tr>
<td>Very soluble</td>
<td>13-18</td>
<td>Oil in water emulsifier</td>
</tr>
</tbody>
</table>

*HLB = (L/T) x 20 (L and T referred to the molecular weight of the hydrophilic (sucrose) part of the molecule and the total molecular weight, respectively)*

Sucrose esters have a wide variety of applications. SE has excellent non ionic surfactant and emulsifier properties that are desirable and promising in food, personal care, detergent, bleaching booster, cosmetic, fine chemical, oral-care and medical applications\(^93,97\). Besides this, they have received considerable attention due to their recent availability in commercial quantities, together with their tasteless, odourless, nontoxic, biocompatible, biodegradable and noncumulative characters\(^98,99\). SEs were approved in 1959 for use as food
additives in Japan\textsuperscript{90}. They are mild toward the skin and eye and possess lower hemolytic activity than many other types of surfactants. However, depending on the nature of the hydrophobic moiety, some sugar-based surfactants possess rather high haemolytic activity. Sucrose esters have been studied for effective preservation of the quality of fresh produce\textsuperscript{100}. Phosphorylated sucrose stearate showed a higher solubility and better emulsifying properties than sucrose stearate and improved the thermal behaviour of potato starch by increasing the gelatinization temperature, decreasing the viscosity and inhibiting retrogradation\textsuperscript{101}.

Fatty acid esters of mono- and di-saccharides, produced commercially by Mitsubishi-Kagaku (Tokyo, Japan) and Sisterna PV (Roosendaal, Netherlands), are effective emulsifiers found in a variety of food, cosmetic, and pharmaceutical products such as chocolate, toothpaste, lotions, shampoo, and lipstick\textsuperscript{87,102,103}. They possess excellent antimicrobial activity as well\textsuperscript{104}. Some possible applications for sucrose based polymers are drug delivery systems, dental medicine, bioimplants, contact lenses, and tissue engineering\textsuperscript{105,106}. The most common pharmaceutical application of SE is for the modification of bioavailability, often with the hot-melt method. Use of SE as surfactants in the development of microparticulate systems for parenteral delivery of protein and gene medicines was investigated\textsuperscript{107}.

SE has shown remarkable use as surfactant in stabilized synthesis of nanoparticles. Huang\textsuperscript{108} synthesised indium sulfide nanorods in water-in-oil (w/o) microemulsion system using food grade SE as biosurfactant. Titanium dioxide nanoparticles were prepared via hydrothermal processing route, which utilized SE as a stabilizing agent\textsuperscript{109}.

Sucrose esters are more soluble in t-pentanol than glucose esters. Dimethyl sulfoxide provides good solvency, especially in the case of glucose and sucrose monoesters\textsuperscript{110}. Sucrose esters display significant activity against several clinical isolates. They have increasing interest due to advantages with regard to the performance, the consumer health and the environmental compatibility compared to petrol-derived standard products\textsuperscript{62}. They have antibacterial properties and can also be used as lubricants\textsuperscript{97}. SE also shares a number of insecticidal properties with other surfactant\textsuperscript{111}. SEs composed of C\textsubscript{6}-C\textsubscript{12} fatty acids have desirable insecticidal properties against many soft-bodied arthropod pests\textsuperscript{112}. Sucrose esters are currently used as additives in the food industry which makes them especially attractive as safe and effective insecticides. The combination of particular characteristics such as emulsifying, anti-adhesive (inhibition and disruption of biofilms formed in food contact surfaces) and antimicrobial activities presented by sucrose esters suggests potential application as multipurpose ingredients or additives\textsuperscript{113}.
ii) Sucrose polyesters (SPE) as fat substitute

SPE has physical and organoleptic properties similar to those of cooking and frying fats and are digested as a blend of sucrose and fatty acids in the stomach. Olestra, a non-caloric fat substitute, is a SPE with moderate to high degree of substitution (six or more fatty acids per sucrose molecule) and has been developed by Proctor and Gambel in the early 1970s and marketed under the brand name Olean. It has been approved by the FDA as a food additive used in preparing low-fat deep-frying foods such as savoury snacks. These compounds are lipophilic, nondigestible and nonabsorbable molecules with physical and chemical properties similar to those of triglycerides, but it is not digestible by lipolytic enzymes.

1.3 Epoxidation of vegetable oils and fatty acids

Epoxidation is the reaction (Fig. 1.5) between double bonds in olefinic compounds (unsaturated fatty acid, alkyl ester, or oil) and organic peroxy acid \([RC(=O)OOH, \text{ oxygen transfer reagent}]\) to obtain (three-membered) cyclic ethers called epoxides. The reaction is catalysed by homogeneous catalysts such as \(H_2SO_4, p\)-toluene sulfonic acid, heterogeneous catalysts such as transition metals of variable valence, acidic ion exchange resin or enzymes. The peracid is either preformed or prepared in situ by equilibrium reaction (Fig. 1.5) between hydrogen peroxide (preferably high strength e.g. 70% w/w) and carboxylic acid [formic or acetic acid or other acids]/ corresponding anhydride or acid chloride. The carboxylic acid is regenerated after epoxidation which proceeds by a concerted mechanism, giving cis stereospecific addition (Fig. 1.6). Thus, a cis olefin leads to a cis epoxide and a trans olefin to a trans epoxide. For example, epoxidation of oleic acid generates cis-9, 10-epoxy stearic acid, while that of linoleic acid gives a mixture of two cis, cis diastereoisomeric bis- epoxides. The carboxylic acid produced is a stronger acid than the strongly hydrogen bonded peracid and may lead to subsequent ring opening reactions especially in the case of formic acid producing dihydroxy and hydroxy carboxylates as byproducts. Hence complete epoxidation is never achieved in the acidic medium.

\[
\text{RCOOH} + \text{H}_2\text{O}_2 \xrightarrow{H^+} \text{RCOOH} + \text{H}_2\text{O}
\]

\[
\text{RCOOH} + \text{H}_3\text{C} = \text{CH}_3 \xrightarrow{\text{RCOOH}} \text{H}_3\text{C} - \text{O} - \text{H}_3\text{C} \text{CH}_3 + \text{CH}_3
\]

Fig. 1.5 In situ peracid epoxidation reaction
1.3.1 The performic/ peracetic epoxidation process

The industrial scale epoxidation process, referred as “Prileschajew reaction”, is most frequently carried out with preformed or in situ generated peroxyacetic acid or peroxyformic acid due to their low cost (particularly the peracetic acid process) and easy availability\textsuperscript{119,120}.

Moreover epoxidation with peracids is irreversible (if the acid does not contain admixtures). On the other hand, problems related to this method are associated with the strongly exothermic character of this reaction and the risk of explosion resulting from the necessity of operations with concentrated solutions of peracids. These problems imply the necessity for strict control of temperature and reaction time. The in situ generation of peracids is mostly preferred because, when the organic peroxyacid is preformed, there are some safety issues associated with its storage since the concentrated peroxyacid is unstable and explosive\textsuperscript{121,122}. Moreover the in situ process operates with a lower concentration of aliphatic acids. On the other hand, the presence of an acid during in situ epoxidation causes the opening of the oxirane ring with formation of undesirable secondary products. In ex situ process, the acid is eliminated from preformed peracid by neutralizing it with a buffer or filtering. With preformed peroxyacetic acid, the conversions, yields and selectivity were higher than those with the in situ formed peroxyacetic acid.

The rate of generation of peroxyformic acid is much greater than that of peracetic acids. Formation of peroxyacetic acid requires an acidic catalyst such as sulfuric acid\textsuperscript{123}. Between the in situ-generated performic and peroxyacetic acid, latter has certain advantages such as need of minimum amounts of reactants in the preparation of epoxidizing reagent and convenience and safety of preparation, handling and stability of peroxyacetic acid at moderate temperatures\textsuperscript{124}. Patwardhan et al\textsuperscript{125} worked on the epoxidation of cottonseed oil using in situ generated peracetic/ performic acid catalysed by liquid inorganic acid. While the rate of formation of oxirane was higher with formic acid, acetic acid was more effective oxygen carrier, promoting the transport of the oxygen from the aqueous phase to the oil phase\textsuperscript{126}. It also functions as a catalyst in the formation of the oxirane ring\textsuperscript{127}. H$_2$SO$_4$ was found to be the most efficient and effective catalyst. But being strong acid, it leads to many side reactions such as oxirane-ring opening to diols, hydroxyesters, estolides and other dimer...
formations. Furthermore it causes the equipment corrosion and must be neutralized and removed from the end product\textsuperscript{128}. Ikhuoria et al\textsuperscript{129} observed that the \textit{in situ} peracetic acid epoxidation of the methyl esters of \textit{parkia biglobosa} seed oil could be carried out in a moderate temperature range of 50-70°C. Peracetic acid resulted in a 10\% higher conversion of double bonds to oxirane\textsuperscript{116} and caused the lower amount of undesirable products formed over that by performic acid. An explanation for this is that due to the very high activity of the formic acid, the hydrogen peroxide is rapidly decomposed leaving the batch oxygen depleted\textsuperscript{37}. Cationic ion-exchange resins are versatile heterogeneous catalysts and offer several advantages over the homogeneous acid catalysts. Use of acidic ion exchange resin catalysts would reduce corrosion problem, avoid disposal of strong acids, and present better product recovery. The catalyst can be recycled, shows better selectivity, and avoids side reactions\textsuperscript{130}. However the rate of resin catalysed epoxidation slows down in comparison to that of homogeneous epoxidation. The heterogeneous method seems to be tedious due to the difficulty of separating the product from the resin.

\subsection{1.3.2 Other techniques of epoxidation}

A cheap and green epoxidiser would be molecular O\textsubscript{2}. But when used in the epoxidation of vegetable oil, it leads to the degradation of the oil to low molecular weight volatile compounds such as aldehydes and ketones as well as short chain dicarboxylic acids\textsuperscript{131}. Organic peroxo acids, other than peroxyformic or peroxyacetic acids, may be more convenient in the laboratory or for small-scale reactions. These include the peroxo acids derived from trifluoroacetic, lauric, benzoic, m-chlorobenzoic acids, and m-nitrobenzoic acid. Monoperoxy acids derived from succinic, maleic, and phthalic anhydrides can also be used. The order of reactivity of some peracids is: m-chloroperbenzoic > performic > perbenzoic > peracetic; electron withdrawing groups promote the reaction. Some of these can be safely stored at 0-20°C to avoid hazards of its decomposition. Small scale reactions are carried out with m-chloroperbenzoic acid in a halocarbon or aromatic solvent, in the presence of bicarbonate to neutralize the carboxylic acid as it is formed\textsuperscript{132}.

Recent studies have attempted enzymatic procedures to improve the efficiency of epoxidation under milder conditions that minimize the formation of byproducts. Chemo-enzymatic epoxidation\textsuperscript{133} uses the immobilized lipase from \textit{Candida antartica} (Novozym 435) to catalyze conversion of fatty acids to peracids with 60\% hydrogen peroxide. The fatty acid is then self-epoxidized in an intermolecular reaction. The lipase is remarkably stable under the reaction conditions and can be recovered and reused 15 times without loss of activity. Competitive lipolysis of triacylglycerols is inhibited by small amounts of fatty acid,
allowing the reaction to be carried out on intact oils\textsuperscript{134}. Rapeseed oil with 5\% of rapeseed fatty acids was epoxidised in 91\% yield with no hydroxy byproducts. Sunflower, soybean, and linseed oils have been satisfactorily epoxidised by this route using 35\% hydrogen peroxide with 5 mol\% of free fatty acid\textsuperscript{134} and in a batch stirred tank reactor at atmospheric pressure\textsuperscript{135}. Corn oil rich in oleic and linoleic acids, was also epoxidized in a similar manner but using stearic acid as an active oxygen carrier\textsuperscript{136}. Methyl esters are also epoxidized without hydrolysis under these conditions.

Epoxidation is also feasible with dimethyl dioxirane (DMDO), made from potassium peroxymonosulfate (KHSO\textsubscript{5}) and acetone. The most common of inorganic peroxides is nitrile hydrogen peroxide, which catalysed by a transition metal catalyst\textsuperscript{131}. Halohydrines, using hypohalous acids (HOX) and their salts as reagents, are also used for the epoxidation of olefins with electron deficient double bonds. But the process is not ecofriendly.

Different novel approaches to epoxidation have recently been reviewed\textsuperscript{137,138}. Compounds of second-row transition metals- rhodium and ruthenium and the oxides of rhenium and tungsten have attracted particular interest as catalysts to affect the epoxidation of olefins, some with excellent regio-, stereo- and enantio- selectivities. Silver, however, produces very low rates of double bond conversion and is also only effective on very simple ethylenic substances. Methyltrioxorhenium (MTO, MeReO\textsubscript{3}) or tungstates catalyses direct epoxidation by hydrogen peroxide. MTO reacts with hydrogen peroxide to give organorhenium peroxo complexes. The reaction is carried out in presence of large excess of nitrogenous bases, particularly pyridine under biphasic conditions, avoiding acidic conditions detrimental to high epoxide yield and uses less concentrated hydrogen peroxide (30\%) than other methods\textsuperscript{139}. This method epoxidized soybean\textsuperscript{140} and metathesized soybean oil in high yield\textsuperscript{141} with higher product selectivity and catalyst lifetime. The epoxidized metathesized oil was more stable to polymerization than that produced using m-chloroperbenzoic acid, presumably because it was free of acidic impurities. Hyeon et al\textsuperscript{142} fabricated molybdenum oxide nanoparticles incorporated into a mesoporous silica shell that are coated on dense silica-coated magnetite nanoparticles and demonstrate a magnetically recyclable epoxidation catalyst. Alumina catalysed sol-gel process was evaluated for the epoxidation of unsaturated fatty esters using anhydrous or aqueous hydrogen peroxide as oxidant and ethyl acetate as solvent. The alumina shows a good catalytic activity and excellent selectivity towards the epoxides. The sol-gel alumina was more efficient and when using aqueous hydrogen peroxide, it could be recycled several times\textsuperscript{143}. None of these methods have yet found feasibility at industrial scale.
1.3.3 Influence of reaction parameters on extent of epoxidation and kinetic and thermodynamic modelling of epoxidation

Epoxidation is a consecutive reaction and its success depends on the control of available conditions for minimisation of opening the rings. The rate of performic acid production, for ex situ process, is at least 4 X 10^4 faster than the rate of epoxidation. This means that whenever a performic acid molecule reacts, another performic acid molecule is generated before any further epoxidation occurs. On the other hand, peracids are unstable, and the reaction is exothermic. The concentration of peracid is therefore kept low by using a low concentration of the carboxylic acid either in the neat oil or in a hydrocarbon solvent. Industrial epoxidation is conducted in two-phase polar (aqueous H_2O_2)-organic (oil plus solvent) systems. The presence of an inert solvent (e.g. xylene, toluene) in the reaction mixture appeared to stabilize the epoxidation product and minimize the side reaction such as the opening of the oxirane ring, especially at higher temperatures. It is important to minimize the presence of protons originating from either the acid or the catalyst and work at low temperatures. Ring opening cannot be totally avoided, but proper control may be attained by working at low temperatures, say 20-35°C. The progress of the epoxidation reaction, as measured by the changes of the hydroxyl value, iodine number and epoxy number, is used to estimate the fractional conversion, yield, and the selectivity of transformation to epoxidized oil/ fatty acids/ ester. The structures of the products are confirmed by thin layer chromatography (TLC), fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) analysis.

The influence of the several reaction parameters such as temperature, hydrogen peroxide: peracid: vegetable oil molar ratio, type of peracid, type and loading of catalyst, stirring speed and reaction period on epoxidation rate as well as the oxirane ring stability for the in situ inorganic acid catalysed (homogeneously catalysed) peroxyacid epoxidation of rapeseed oil, mahua oil (Madhumica indica), cottonseed oil, soybean oil and jatropa oil were examined. Elevation of the temperature from 30 to 60°C caused a decrease of the iodine number, while the value of the epoxy number rapidly decreased above 60°C for the formation of epoxidised rapeseed oil. Increasing temperature showed a favorable effect on the formation of peracetic acid during the epoxidation of mahua oil. Acetic acid was found to be superior to formic acid for the in situ cottonseed oil epoxidation. In general, with an increase in hydrogen peroxide-to-ethylenic unsaturation molar ratio, there was a progressive increase in the rate of oxirane formation. However, the correlation between decrease in the final iodine value and the corresponding increase in the final oxirane value were relatively
less when the ratio was increased beyond particular magnitude, specific to individual oils. This may be attributed to the higher hydrogen peroxide concentration leading to an accelerated rate of oxirane ring decomposition. To attain the maximum oxirane oxygen content in peroxyacetic acid epoxidation, the optimum level of the acetic acid should be used where both the effects (catalytic effect counteracting hydrolysis) are balanced considering the amount of acid required in the formation of peracetic acid. The maximum reaction conversion was 83.3% for the epoxidation of soybean oil and 87.4% for the epoxidation of jatropha oil. It was possible to obtain up to 78% relative conversion to oxirane with very less oxirane cleavage by in situ sulfuric acid catalysed epoxidation of cottonseed oil. The order of effectiveness of catalysts was found to be sulfuric acid > phosphoric acid > nitric acid > hydrochloric acid. For a two-phase epoxidation reaction mixture, different solubility of peracid in the organic phase can have a large effect on the kinetics. Thus to safely avoid mass and heat transfer effects, a stirring speed of higher order feasible with the given system should be chosen. Okieimen et al.\textsuperscript{121} have shown that the negligible oxirane cleavage and almost complete epoxidation of rubber seed oil by in situ peroxyacetic acid process could be achieved.

In a similar manner, the effect of different reaction variables on heterogeneous in situ cationic exchange resin- Amberlite IR-120 catalysed peracid epoxidation of soybean oil\textsuperscript{148}, jatropha oil\textsuperscript{124} and castor oil\textsuperscript{149} was evaluated. With an acidic ion exchange resin as the catalyst for the epoxidation of vegetable oils, the porous structure of the solid catalyst and the size of the natural unsaturated triglycerides were found to minimize side reactions and thus improve selectivity\textsuperscript{150}. At lower temperatures (30, 50 and 70°C), peroxyformic acid was found to be more efficient, while at higher temperature (85°C), peroxyacetic acid was equally good and an optimum in the ion exchange resin catalyst reactivity was observed at 70°C for the formation of epoxidised jatropha oil. The extent of the side reaction is negligible with peracetic acid in the entire temperature range and somewhat higher with performic acid at 85°C for epoxidation of castor oil. The optimal conditions (91% conversion, 5.99% epoxide content in product) for peracetic epoxidation of soybean oil were found to be: 0.5 mole of glacial acetic acid and 1.1 mole of hydrogen peroxide (30%) per mole of ethylenic unsaturation, 75°C, 8 hrs, 5 wt% of the resin catalyst\textsuperscript{148}.

The rate law that holds for epoxidation of all oils and FAME is shown in Eq. 1.1:

$$ r = \frac{d[D_{B}]}{dt} = k \left[D_{B}\right] [PFA] \quad \text{Eq. 1.1} $$
Where \( r \) is the rate of disappearance of carbon-carbon double bonds, \([DB]\) is the concentration of double bonds, \([PA]\) is the concentration of peracid and \( k \) is the second-order rate constant. For *ex situ* and sometimes for *in situ* process, the epoxidation reaction can be assumed to be pseudo-zero order in peracid concentration because the rate of formation of peracid is much faster than the rate epoxidation. The epoxidation and ring opening for *in situ* epoxidation of anchovy oil with partially preformed peracetic acid in the presence of a resin catalyst\(^{151}\) were described, by applying the principle of the stationary state, by a pseudo first-order reaction. Two studies of the kinetics of the *in situ* epoxidation of oleic acid with hydrogen peroxide and acetic acid and of methyl esters of palmolein by performic and peracetic acid, both carried out in the presence of sulfuric acid as a catalyst, concluded that the rate-determining step of the epoxidation process was the formation of peracetic (or performic) acid\(^{145,152}\). Rangarajan et al\(^{120}\) reported kinetic parameters for the *in situ* epoxidation of soybean oil by peracetic acid, again in the presence of sulfuric acid as the catalyst, but treated it as a two-phase system. Significantly higher rates were obtained in kinetically controlled regimes. Jankovic et al\(^{153}\) proposed the mathematical model that describes the kinetics of reaction systems for the *in situ* epoxidation of unsaturated fatty acid esters or triglycerides with organic peracids. Kinetic studies of epoxidation of soybean oil with peroxyacetic acid and peroxyformic acid have been reported and found to be pseudo-first order with respect to both double bonds as well as peroxy acid\(^{37}\).

The magnitude of rate constants (\( k_{\text{epo}} \)) in cm\(^3\)mol\(^{-1}\)s\(^{-1}\) and the energy of activation (\( E_a \)) in Kcal/mol for conc. sulfuric acid catalysed preformed (*ex situ*) peracetic epoxidation of undecylenic acid, methyl undecylenate, and ethyl undecylenate undecylenic acid over 25-35\(^0\)C were found to be- 0.06-0.09 and 20.78, 0.096-0.12 and 6.95 and 0.046-0.11 and 15.34, respectively\(^{130}\). The apparent activation energy using Arrhenius relationship, for the *in situ* formation of epoxidised jatropha oil was found to be 53.6 kJ/mol\(^{124}\) which compared well with the corresponding value of 48.6 kJ/mol, as obtained by\(^{154}\) for a similar acidic ion exchange resin catalysed epoxidation of a vegetable oil. The epoxidation of castor oil with performic and peracetic acid generated *in situ* in presence of cation exchange resin (Amberlite IR-120) was found to be first order with respect to the conversion of ethylenic unsaturation. The rate constants for the epoxidation with peracetic acid were 0.067, 0.184, 0.55, and 1.12 (hr\(^{-1}\)) at 30\(^0\)C, 50\(^0\)C, 70\(^0\)C and 85\(^0\)C, respectively, while those for the performic acid were 0.125, 0.287, 0.645, and 0.981 (hr\(^{-1}\)). Activation energies of the peracetic acid and performic acid epoxidation were found to be 48.2 kJ/mol and 35.4 kJ/mol, respectively\(^{149}\). The kinetic modelling of Novozym 435 catalysed epoxidation of oleic acid
based on ternary complex mechanism was reported. Following kinetic parameters were deduced at \(30^0C\): \(V_{\text{max}}\) = maximum epoxidation velocity = \(2.229 \times 10^5 \text{mmol/L/min/g enzyme}\) and \(K_{iA}\) = dissociation constant for enzyme-oleic acid complex \(59.986-65.618\) (mmol/L/g enzyme). At low temperatures, the rate of epoxidation was faster than the rate of deactivation of the enzyme by hydrogen peroxide.

**Table 1.3** provides the kinetic constants \((k_{\text{epo}} \text{ and } E_a)\) and thermodynamic parameters [enthalpy of activation-\(\Delta H\), average entropy of activation-\(\Delta S\), and free energy of activation-\(\Delta G\) ] reported by different investigators for sulphuric acid catalysed peracetic acid *in situ* epoxidation of different oils/ esters. These thermodynamic data show that the epoxidation is a non-spontaneous process.

In Eq. 1.1, if triglyceride structure is going to have any effect on epoxidation reaction kinetics, the only parameter that can be affected is the rate constant implying likely influence of the FA composition on the value of the rate constant. The rate constants of noncatalysed, *ex situ* epoxidation were determined by reacting preformed formic acid with a number of oils (cottonseed/ corn/ olive/ soybean oil etc.) model triglycerides (triolein, trilinolein) and model fatty acid methyl esters (FAME). In triglycerides, the double bonds of oleic acid and linoleic acid were equally reactive, and the double bonds of linolenic acid were approximately three times more reactive than oleic and linoleic acids. For FAME, the rate constants of epoxidation increased as the level of unsaturations increased. Furthermore, the rate constants of epoxidation for the FAME were higher than their respective triglycerides. These results showed that the FA composition had a significant effect on the value of the epoxidation rate constant and were interpreted on the basis of the steric and electronic effects on epoxidation kinetics. The double bonds further from the glycerol center are more reactive than double bonds near the glycerol center and double bonds on different FA have different reactivities. Steric factors inherent in the triglycerides structure reduce the reactivity of the unsaturated sites in comparison to the same site on FAME. As the number of double bonds increases, the electron density increases, this causes an increase in the rate constant for epoxidation of linolenic acid. These results were used to derive a model that predicts the epoxidation kinetics of oils from their FA composition. The relative rates of epoxidation for oleic, linoleic and linolenic acids are 1.0, 1.0 and 1.7, respectively. The triacylglycerols are slightly more reactive than the acids with values of 1.9, 3.0 and 4.9, respectively.

Twelve epoxidised oil derivatives based on rubber seed oil, *Madhuca* oil (*Mee* oil) and Neem oil and their hydrolysed products were prepared by optimised conditions on a comparatively large scale without solvent extraction procedures. It was found that more than
80% of the reaction was completed within three hours at 60°C. The level of epoxidation could be controlled reasonably by limiting the reagents. The solubility parameter values calculated from the molar attraction constant values \(G\), using Small’s equation, were comparable with those of conventional plasticizers used in the PVC industry\(^{156}\).

Table 1.3 Kinetic and thermodynamic parameters for sulphuric acid catalysed peracetic acid in situ epoxidation of different oils/esters

<table>
<thead>
<tr>
<th>Oil/esters</th>
<th>Kinetic constants</th>
<th>Thermodynamic parameters</th>
<th>Literature reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_{\text{epo}}, \text{L mol}^{-1}\text{s}^{-1})</td>
<td>(E_a)</td>
<td>(\Delta H)</td>
</tr>
<tr>
<td>Cotton seed oil</td>
<td>0.39-5.42 X 10^{-6} (temp. range 30-75°C)</td>
<td>11.7 kcal/mol</td>
<td>11.0 kcal/mol</td>
</tr>
<tr>
<td>Mahua oil</td>
<td>0.2-6.8 X 10^{-6} (temp. range 30-85°C)</td>
<td>14.5 kcal/mol</td>
<td>13.8 kcal/mol</td>
</tr>
<tr>
<td>Methyl esters of parkia biglobossa seed oil</td>
<td>3.5 X 10^{-7} (temp. range 50-70°C)</td>
<td>51.963 kJ/mol</td>
<td>13.8 kJ/mol</td>
</tr>
</tbody>
</table>

1.3.4 Ring opening and synthesis of multifunctional derivatives

A lot of trifunctional compounds (introduction of hydroxyamines, hydroxynitriles, diols, etheralcohols, hydroxyalkylamides etc. in FA or triglycerides) are the result of splitting of oxirane ring by nucleophilic compounds (secondary amines, hydrogen cyanide, water, alcohols, amides etc.). Applications for these interesting oleochemicals have not yet been fully investigated.

The three-step synthesis of several diesters from commercially available oleic acid and common fatty acids was reported\(^{157}\). The key step of ring opening of epoxidized oleic acid with different fatty acids (octanoic, nonanoic, lauric, myristic, palmatic, stearic and behenic acids) was achieved using \(p\)-toluenesulphonic acid (PTSA) as catalyst. The esterification reaction of these compounds with octanol was further carried out in the presence of \(H_2SO_4\) giving diester compounds. This study described a systematic approach to improve the low temperature pour property of oleic acid derivatives. Salimon et al\(^{24}\) also reported the oxirane ring opening of epoxidized oleic acid using behenic acid and PTSA as catalyst followed by esterification with octanol and 2-ethylhexanol to form diesters for
industrial biolubricant applications. Moser\textsuperscript{158} also reported the preparation of branched chain ethers from oleic acid in a three-step synthesis. Esterification of oleic acid was followed by the epoxidation of double bond and then a ring-opening step by an alcohol (alkyl: propyl, isopropyl, octyl, 2-ethylhexyl) using propionic and octanoic acid medium without the need for either solvent or catalyst.

![Fig 1.7 Ring opening of epoxidised oils](image)

For the production of lubricants from vegetable oils, the oils are first epoxidized, and then the oxirane ring is opened with either acetic acid or a low chain aliphatic alcohol like methanol or ethanol\textsuperscript{159}. Epoxidized oils were ring opened by a one-pot, one-step process by using a predetermined amount of allyl alcohol mixed with tetrafluoroboric acid catalyst. Allylic double bonds were successfully incorporated into triglycerides of epoxidized oils through a ring-opening nucleophilic addition reaction of allyl alcohol. The reaction is facile with high conversion under mild conditions\textsuperscript{160}. The epoxidation of natural oils and subsequent ring opening with acrylic acid has been well studied\textsuperscript{161}. Acrylation kinetic model that predicts rate constants from fatty acid distributions in the oil were established\textsuperscript{144}. Thus, the rate constant of acrylation increased as the number of epoxides per fatty acid decreased. Multiple epoxides per fatty acid decrease the reactivity of the epoxides because of steric hindrance effects and the oxonium ion, formed as an intermediate during the epoxy-acrylic acid reaction, is stabilized by local epoxide groups.

Ring-opening polymerization of epoxidized soybean oil (ESO) catalyzed by boron trifluoride diethyl etherate (BF\textsubscript{3}.OEt\textsubscript{2}) in methylene chloride was conducted in an effort to develop useful biodegradable polymers\textsuperscript{162}. Epoxidized diethanolamides were synthesized by reacting diethanolamine (DEA) with mixture of epoxidized palmolein (40% w/w) and refined
bleached deodorized palmkernel olein (60% w/w) at 1:3 molar at 80°C for 5 hrs and continued at 110°C for another 4 hrs of reaction time. Synthesized diethanolamides with high content of epoxides were reacted with isocyanate in the presence of AlCl₃-THF complex catalyst to produce oxazolidone linkages in polyurethane network. The rigid polyurethane foam produced is of better quality as compared to the commercially available foam.

The kinetic study on the oxirane cleavage of palmolein methyl ester has been reported. The first degradation reaction is first order with respect to the epoxide concentration and second order with respect to the solvated acetic acid [kₐₐ(70°C) = 4.27 ± 0.12×10⁻⁵ l²mol⁻²min⁻¹; Eₐₐ = 12.9 ± 0.64 kcal mol⁻¹]. The degradation increases notoriously the lower the pH of the reacting media is; the increase is directly proportional to the concentration of protons, as is usually found in homogeneous catalysis (for very low pH, the reaction is almost instantaneous). Likewise, the degradation reaction with peracetic acid is first order with respect to the epoxide [kₚₚₐₐ(70°C) = 4.31 ± 10⁻⁴ l²mol⁻²min⁻¹; Eₚₚₐₐ = 10.6 ± 0.38 kcalmol⁻¹] and it also increases linearly with proton concentration. Although the specific attack on the ring by the peracid is almost 10 fold harsher, acetic acid is constantly being regenerated during the industrial process, so that its concentration is always far larger than that of peracetic acid. Thus, under process conditions the degradation of the oxirane ring is mostly caused by the carboxylic acid. A systematic investigation of the impact of the various consecutive reactions of oxirane ring-opening on the yield of the epoxidised soybean oil was carried.

1.3.5 Applications of epoxidised oils and fatty acids

Oils, mainly soybean and linseed, are epoxidized on an industrial scale (0.2 MMT per year) for utilization as stabilizers and plasticizers for PVC polymers. Epoxidised oils are also used as plasticizer in the production of packing materials such as wrapping foils. Plasticizer is an additive for plastic formulations to enhance their plastic workability and flexibility and is generally produced from petroleum derivatives such as phthalate compounds. The plasticizing efficiency of epoxidised oils is equivalent to that of dioctyl phthalate. Besides this, epoxidised oils also improve UV light and heat stability of PVC plastic due to the presence of the oxirane rings. The typical stabilization action for PVC is derived from the fact that the reactive epoxide groups scavenge hydrogen chloride produced by the degradation of the PVC polymer, interrupt the formation of polyene sequences in the polymer and retard the apparition of discoloration. They are generally regarded as secondary stabilizers used to enhance the effectiveness of metal soaps. The marked effect on the thermal stabilization of PVC by epoxidised oils requires the synergistic
The presence of metallic soaps\textsuperscript{172,173}. The esterification and etherification reactions which occur with allylic chlorine groups in PVC provide an explanation for the synergism observed in the stabilization of PVC containing a combination of an epoxy compound with metal soap\textsuperscript{168,171}. Epoxidized oils transesterified with low-molecular weight alcohols are also used as plasticizers of polyvinyl chloride\textsuperscript{174-176}. In particular, methyl esters of epoxidized soybean oil represent a renewable substrate that is readily converted into surfactants, fuel additives, and other industrial products\textsuperscript{177}.

A significant lubricant market of some nine million metric tons per year of industrial and automotive lubricants exists and there has been a constant demand for environmentally friendly or green lubricants. As lubricants, vegetable oils possess superior lubricity, good anticroosive properties, better viscosity-temperature characteristics and low evaporation loss which are important in industrial applications such as rolling, cutting, drawing, quenching operations, and greases\textsuperscript{159,178}. Their low volatility and narrow range of viscosity changes with temperature are due to the high molecular weight of the triglyceride molecule. Polar ester groups in vegetable oils are able to adhere to metal surfaces and, therefore, possess good boundary lubrication properties. In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules. From the environmental point of view, their importance is evident especially in areas of total loss lubrication, military applications, and in outdoor activities such as forestry, mining, railroads, dredging, fishing and agriculture hydraulic systems. In spite of these facts, vegetable oils currently provide only a fraction of the lubricant market due to the poor stability and low temperature properties. For the production of lubricants from vegetable oils with improved oxidation stability and pour point characteristics, the oils are first epoxidized, and then the oxirane ring is opened with either acetic acid or a low chain aliphatic alcohol like methanol or ethanol\textsuperscript{159} followed by the reaction of the epoxide function with linear and branched-chain alcohols. Epoxy esters\textsuperscript{144}, due to the overall good lubrication characteristics, are being actively investigated as biolubricants. Salimon et al\textsuperscript{24} reported the oxirane ring opening of epoxidized oleic acid using behenic acid and \textit{p}-toluenesulfonic acid as catalyst followed by esterification reaction with octanol and 2-ethylhexanol to form diesters for biolubricant industrial applications. Epoxidized soybean oil functionalized with diamine is an excellent antioxidant and lubricant, and has been proven as an antifriction agent. Because of its amphiphilic character it is added to base grease oils to improve their application properties\textsuperscript{179}. Activity of epoxidised oils is essentially related to the amount of oxirane oxygen, but the plasticization, lubrication and cost parameters play a role in their selection and use.
Due to the high reactivity of the oxirane ring in epoxidized oils, they are used as renewable raw materials for manufacturing such intermediate products as alcohols, glycols, alcoxyalcohols, hydroxyesters, N-hydroxalkylamides, mercaptoalcohols, hydroxynitriles, alkanolamines, and carbonyl compounds\textsuperscript{131,180}. Thus, epoxidised oils/ fatty acid derivatives are used as intermediates for a large number of commodities such as agricultural and pharmaceutical molecules, flavors and fragrances, surfactants, adhesives, sealants\textsuperscript{181-184}. With sodium iodide and an appropriate solvent, epoxy esters are converted to keto esters (RCOCH\textsubscript{2}R’ and RCH\textsubscript{2}COR’). Natural vernolic acid (12, 13-epoxyoleic acid) is being examined as an antitrust additive (as its C\textsubscript{4}-C\textsubscript{6} amides) and as a source of dibasic acids and of high-value products such as the pheromone bombykol (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{2}CH=CH CH=CH(CH\textsubscript{2})\textsubscript{8} CH\textsubscript{2}OH) and the plant wound hormone traumatic acid (HOOC(CH\textsubscript{2})\textsubscript{8}CH=CHCOOH). Limonene epoxide has traditionally been used as a precursor for the synthesis of perfumes, drugs, and food additives\textsuperscript{185}.

Petrochemical based resins such as epoxy, polyester and vinyl ester find more engineering applications because of their advantageous material properties such as high stiffness and strength. However these resins have serious drawbacks in terms of biodegradability, initial processing cost, energy consumption and health hazards. Renewable epoxy esters can be used as diluents in paints and so replace volatile organic solvents. Reaction of epoxidised oils or fatty acids with acrylic acid (CH\textsubscript{2}=CHCOOH) gives an acrylate which can be cured by exposure to UV photoinitiated free radical or cationic polymerization\textsuperscript{186-188}. Polyhydroxy compounds produced by reaction of epoxides with diols and triols (glycerol) serve as a source of polyurethanes through reaction with isocyanates\textsuperscript{155}. Green nanocomposite coatings with excellent film properties and good biodegradability have been obtained with epoxidised soybean and linseed oil and γ-glycidoxypropyl trimethoxysilane\textsuperscript{189}.

1.4 Synthesis and characterization of dimer acids

One finds number of patents on polymers based on vegetable oils\textsuperscript{190} as number of different dimers and oligomers are produced from fatty acids and alcohols. The term dimer acid\textsuperscript{191-195} is applied to the branched-chain acyclic or cyclic dicarboxylic acids (predominantly the C\textsubscript{36}) formed by the thermal (260-400\textdegree{}C) or catalytic (acid activated clay or other cationic catalysts) polymerization reactions of two or more C\textsubscript{18} unsaturated fatty acids or monohydrmic esters of semi-drying oils such as tall oil, sunflower, soybean and rapeseed oils or drying oils such as dehydrated castor oil. Typical manufacturing conditions\textsuperscript{196} are: 4% montmorillonite clay catalyst at 230\textdegree{}C for 4-8 hours under steam pressure. Dimerization is usually carried out
in the presence of a little water (1-2%) to prevent decarboxylation at high temperature. The extent of reaction was determined by measuring changes in refractive index, molecular weight and acid values of the dimerized oil samples. After the desired reaction is complete, the mixture is cooled, a metal complexing agent, usually phosphoric acid, is added and the crude product is filtered. The product is a complex mixture of acyclic, cyclic, and bicyclic C₃₆ dimer acids as the main product (Fig. 1.8), apart from some C₅₄ tricarboxylic trimer acids and higher condensed polymer acids as well as unreacted and structurally modified (e.g. isostearic acid) monocarboxylic acids. The monomers are recovered as overhead product by vacuum distillation. The separation from trimer and higher homologs is achieved by molecular distillation or wiped film evaporator.

![Fig. 1.8 Dimerization of polyunsaturated fatty acid](image)

Other catalysts investigated for this reaction include peroxides, hydrofluoric acid and sulphonic ion exchange resin. The reaction also has been investigated under corona discharge. Catalysis by super acids has received considerable attention in recent years. The sulphate-treated zirconia super acid catalyst has high chemical stability, and being a solid does not pose any corrosion problems. Dimerization of fatty acids derived from dehydrated castor oil and safflower oil was carried out on the sulphate-treated zirconia catalyst and trifluoromethane sulphonic acid (triflic acid) under autogeneous pressure in the temperature range of 160-240°C. Triflic acid was observed to be highly active; however, the product obtained was deeply colored. Zirconia exhibited high activity for the reaction. The important features of this catalyst were the lower cost in comparison to triflic acid, the high selectivity for dimer (low yields of trimer) and no significant coloration of the products.

Anyaogu et al. as well as Boot and Speek have reported the optimum condition for the polymerization of soybean oil to include 350°C, 0.0025% iodine catalyst and a reaction time of 20 min under inert atmosphere. None of these methods has succeeded commercially.

The diversification of the sources of precursors for the production of dimer acids will reduce the pressure on the regular oils which are already in use in many domestic and industrial applications. The physical properties of dimer are affected by the raw materials used in the manufacture, reaction conditions and content of monomer, dimer and trimer.
These branched dibasic compounds possess significantly lower melting points than straight chain structures of similar molecular weight. All the dimer acids are liquid at 25°C, even though their molecular weight is about 560. This phenomenon can be attributed to the presence of large number of isomers which tend to lower the melting point. Dimer and trimer acids as well as monomer acids derived from dimer acid processing are neither flammable nor combustible. Fully saturated dimers have excellent oxidative stability. This and their extended liquid range are exploited in their use as lubricants and cosmetic additives. Dibasic dimer acids react with polyamines to give reactive polyamides as epoxy curing agents in the formulation of anticorrosive coatings and nonreactive polyamides for utilization in printing inks hot melt adhesives and petroleum exploration operations with outstanding chemical, physical and mechanical properties \(^{209}\). Imidazole derivatives are used as corrosion inhibitors and esters as lubricants. Dimer acids also find wide applications as source of polybasic acids for the synthesis of polyester and polyamidoamines. Isostearic acids, byproduct in dimer production, are important intermediates in the production of biodegradable lubricants, emollients, and hydraulic fluids. The scope and potential of the zeolite-catalyzed synthesis of isostearic acids starting from oleic acid is examined \(^{210}\).

1.5 Alkali fusion of castor oils

The broad and versatile use of castor oil is because of its unique structure and comes from its main component, ricinoleic acid (12-hydroxy-9-cis-octadecenoic acid), which represents 90% of the vegetable triglycerides. This triglyceride has three chemical groups subject to modifications: hydroxyl (C\(_{12}\)), C-C double bond (C\(_9\)), and acid carbonyl, giving a variety of derivatives \(^{217}\). The hydroxyl group at 12\(^{th}\) position is so reactive that the molecule can be split at that point by high-temperature pyrolysis and by caustic fusion to yield useful products of shorter chain length. Sebacic acid (1,8-octane-dicarboxylic acid or decanedioic acid), a linear saturated C\(_{10}\) dicarboxylic acid, is manufactured by heating castor oil to high temperatures (about 250°C) with alkali. This treatment results in saponification of the castor oil to sodium ricinoleate that is then cleaved to give capryl alcohol (2-octanol) and sebacic acid (Fig. 1.9).

Although the sebacic acid yields by above route are low, the route has been found to be cost competitive and used commercially by Union Camp in Dover, Ohio and by Hokoku Oil Company, Japan \(^{196}\) for mass production of sebacic acid in either a batch or continuous process. The castor oil or ricinoleic acid and caustic are fed to a reactor at a temperature of 180-270°C, where the ricinoleic acid undergoes the series of reaction with evolution of hydrogen to give disodium sebacate and capryl alcohol. When the reaction is complete, the
soaps are dissolved in water and acidified to a pH of about 6. At this pH, the soaps of monobasic acids are converted to free acids that are insoluble in water. The disodium sebacate is the only partially neutralised to the half acid salt, which is water soluble. The oil and aqueous layers are separated. The aqueous layer containing the half salt is acidulated to a pH of about 2, causing the resulting sebacic acid to precipitate from the solution. It is then filtered, water washed, and finally dried. 2-Octanol, 2-octanone, and sebacic acid were determined by GC and GC/MS analysis, and purity of sebacic acid was further assessed by its acid value (444) and melting point (134ºC). The crystals of sebacic acids are monoclinic leaflets (ρ-1.231). It is only slightly soluble in water even at 110ºC. It is soluble in alcohol and ether but nearly insoluble in benzene.

![Chemical Structure](image)

**Fig. 1.9 Alkali fusion of castor oil**

The mechanism for the conversion of ricinoleic acid to sebacic acid\(^{218}\) is shown **Fig. 1.10**. The first step is the dehydrogenation of ricinoleic acid to a \(\beta, \gamma\)-keto acid, followed by isomerisation of double bond to give \(\alpha, \beta\)-unsaturated keto acid intermediate in the presence of alkali. At elevated temperature, this intermediate should undergo a retro-aldol type of reaction to give a saturated ketone and a \(\omega\)-aldehydo acid in the presence of water. The methyl hexyl ketone takes hydrogen from the first step of dehydrogenation for reduction to form 2-octanol. On the other hand, two possible reactions may take place with the aldehyde of decanoic acid. One reaction is a reversible reaction of hydrogenation (the hydrogen being made available from the first step of dehydrogenation) to form 10-hydroxy decanoic acid, while in the presence of strong alkali at elevated temperature, the \(\omega\)-aldehydo acid would undergo an irreversible oxidation to yield sebacic acid. Since only one mole of hydrogen is available *in situ* after dehydrogenation of ricinoleic acid and the same is likely to get distributed for the subsequent hydrogenation of methyl hexyl ketone and aldehyde of decanoic acid, the presence of suitable catalyst, which may work as oxygen donor, favours the oxidation reaction of aldehyde of decanoic acid. Longer reaction period (such as 13 hrs),
lower temperature range (458-463 K) and use of 1 mol of sodium or potassium hydroxide per ricinoleate promote formation of 10-hydroxydecanoic acid. Using 2 mol of alkali per 1 mol of ricinoleate at 513-549 K and with a shorter reaction cycle produces sebacic acid. Hydrogen was also formed with excess alkali\textsuperscript{219}.

A number of process improvements have been described and include the use of white mineral oil having a boiling range of 300-400\degree C or the use of mixture of cresols\textsuperscript{220}. These materials act to reduce the reaction mixture’s viscosity and thus improve mixing. The normally expected theoretical yields of 2-octanol and sebacic acid from alkali pyrolysis of castor oil containing 84% ricinoleic acid are 35.7 and 43.6\%, respectively. Higher sebacic acid yields are claimed by the use of catalysts such as barium salts\textsuperscript{221}, cadmium salts\textsuperscript{222}, lead oxide and salts\textsuperscript{223}, sodium nitrate\textsuperscript{224} and zinc oxide\textsuperscript{225}. The presence of barium is to provide a process which enables the recovery of sebacic acid without neutralisation of fusion bath. The role of adjuncts in enhancing the yields of the desired products is, however, not very explicit in the literature. Alkali pyrolysis at 280 ± 2\degree C for 5 hrs using an overall ratio of alkali to diluent (white mineral oil) of about 8:27 and 1\% red lead catalyst in a cylindrical reactor yielded 70.1\% 2-octanol and 72.5\% sebacic acid on the basis of their respective theoretical yields\textsuperscript{226}. The oxygen donating effect of \(\text{Pb}_3\text{O}_4\) may play an important role in increasing the yield of sebacic acid by oxidation of aldehyde of decanoic acid and suppressing the other forward reaction of hydrogenation of the aldehyde of decanoic acid to form 10-hydroxy decanoic acid.

Heating and driving chemical reactions by microwave energy has been an increasingly popular theme in the scientific community\textsuperscript{227}. Azcan et al\textsuperscript{228} studied the effect of microwave irradiation on alkali fusion of castor oil using different \(\text{NaOH}/\text{oil}\) ratios (8:15, 12:15, and 14:15), reaction temperatures (473, 493, 503, 513, and 523 K), and reaction times (15, 20, 25, and 30 min) in the presence of 1\% \(\text{Pb}_3\text{O}_4\) catalyst. Maximum yields of oleochemicals were obtained using methylated then presaponified castor oil (sodium ricinoleate), 14/15::\(\text{NaOH}/\text{oil}\) ratio at temperature 513 K and 20 min reaction time.

Sebacic acid finds applications as monomeric and polymeric plasticizers for PVC, dioctyl sebacate for jet engine lubricants and air-cooled combustion engines and polymer intermediates for 6,10 nylons, polyesters and polyurethanes used in adhesives, coatings, fibers, inks and resins. It is also used as a mineral floatation agent and for producing emulsifiers, defoaming and anti-bubbling agents. 2-Octanol (capryl alcohol) is used in plasticizers in the form of dicapryl esters of various dibasic acids\textsuperscript{229}.
Background of present investigations

Structurally, fatty acids and esters closely resemble materials (petroleum hydrocarbons) already recognized and understood by the current chemical industry based on nonrenewable feedstock. Raw material familiarity will be an important component in transitioning the industry from nonrenewables to renewables, and general technology and equipment/plant design present in the chemical industry today can be easily adapted/retrofitted to the production of oleochemicals. Epoxidation of olefins present the glaring example of this transition. Current research efforts in oleochemicals have focused only on biodiesel as an area of investigation which is simply one of many products that are derived...
from the oleochemical unit operations. The state of the art in chemical modification of fatty acids/oils focuses almost entirely on simple, incremental changes at the COOH group of the molecule. Shifting the focus from a single product to the much broader oleochemical platform, as stated under initial para of introduction, is absolutely necessary on the way to the sustainable and economical usage of lipids as renewable feedstock for organic chemical industries. For example, application of mature technologies well known to the chemical industry could lead to some of their traditional building blocks when applied to low value mixed fatty acids. This research work will detail important R&D opportunities for development of different chemical modification technologies for fatty acid/oil conversions.

A key barrier to the oleochemical unit operation is acceptance of a new form of raw material by the chemical industry. The hydrocarbon nature of fatty acids and esters, with appropriate development of new technology, can serve as an important transitional raw material as the chemical industry evolves from nonrenewable to renewable raw materials. However, use of crude oil still dominates the industry, while oleochemistry remains a specialty sideline. This situation, as is the case with any commodity technology, could change radically upon introduction of new conversion technology for the raw materials and a realization of their potential by the chemical industry. Demonstration of that potential and addressing the important barriers in utilization of oils and fats are the objectives of present investigations.

The broad range of vegetable oil sources lead to diverse fatty acid structures. These structural units can be used to introduce new functionality that can be translated into marketplace properties. The major vegetable oil sources in the U. S. are soybean and cottonseed while those for European Union are rapeseed and sunflower oil. The economics of Malaysia is governed by palm and palmkernel oil. India is the largest producer of groundnut oil, castor oil and many native nontraditional oils. Developing of new or optimization of technologies for the invention of next generation products are feasible in the most promising growth areas such as surfactants, lubricants, additives and polymers. Improved products and technology, exhibiting properties deemed of value, will allow capture of a greater proportion of these markets by renewable oils and fats. Research efforts in the areas of transformations related to the COOH group, in present work, is mainly concentrated on process optimization and modeling studies in synthesis of sucrose ester. From a research viewpoint, a great opportunity exists to develop cost effective and efficient technology for the selective structural modification of fatty acid side chains. The chemical transformations in hydrocarbon chain of fatty acids have the additional advantage of being able to draw on the
broad knowledge possessed by the petrochemical industry. Thus it is essential to explore the breadths of the catalytic processes (alkali fusion in present work) available and examine their feasibility. In a similar manner, the examination of unsaturated oils and their transformations (epoxidation, ring opening, Dimerization in present work), which may fulfill the interests of the oleochemical industry, was undertaken.

1. Surfactants and specialty chemicals: An area of potential opportunity is in the production of sucrose ester. These are surfactants based entirely on renewables as starting materials, and are the result of the reaction between a carbohydrate (sucrose) and a fatty acid methyl ester/oil to give an amphiphilic molecule possessing a polar sugar based head group and a long nonpolar oleochemical tail. The research challenge in producing these materials arises in developing technology suitable for the selective reaction of a fatty acid at a single site of the carbohydrate molecule without the requirement of a complex series of protection/deprotection sequences. While there are currently commercial products based on this technology, the materials are mixtures of mono, di, and triesters, which limit their utility to particular applications. Given that the performance of these materials will be based on their structure, process optimization for selective transesterification and modeling studies based on the concepts of Reaction Engineering were the objectives of research investigations.

2. Polymers and coating: Another very large potential market for consumption of fatty acid derivatives is the polymer market. Use of oleochemicals, particularly diacids, as polymer components is known but its share of the total polymer market is very small. The portion of the polymer market is dominated (87%) by materials such as adipic or terephthalic acid, while use of oleochemically derived diacids accounts for only 0.5% of the total. Displacing the commodity acids will be difficult; however, the use of oleochemical diacids offers access to an interesting suite of properties including elasticity, flexibility, impact strength, hydrolytic stability, hydrophobicity, lower $T_g$, and flexibility. In present research, synthesis of diacids such as sebacic acid by catalytic alkali fusion of castor oil and dimer acids by catalytic thermal polymerisation of polyunsaturated oils and fatty acids/esters have been carried.

3. Additives and lubricants: The market opportunity exists in the production of biolubricants from oleochemicals. Petrochemically derived lubricants possess an environmental problem in that they are often released during their use, for example, in various engines, metal working, chain saws, etc. Epoxidation of the double bonds in fatty acids is an area of current interest, as oil epoxides have utility as additives for PVC. Mustard oil has been epoxidized and ring opening studies have been carried to obtain biolubricants.
The kinetic and thermodynamic studies on epoxidation and ring opening reactions and comparative engineering evaluations of different reactor options were also focused.

References

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