2. RECENT TRENDS IN OLEOCHEMISTRY

Oleochemistry is an important branch of chemistry and privileged part in organic chemistry, medicinal chemistry and polymer chemistry, encompassing the diverse range of biological and industrial applications. Thus, Oils and fats of vegetable and animal origin have been the most important renewable feedstock of the chemical industry in the past and in the present. A tremendous geographical and feedstock shift of oleochemical production has taken place Worldwide from tallow to palm oil. It will be important to introduce and to cultivate more and new oil plants containing fatty acids with interesting and desired properties for chemical utilization while simultaneously increasing the agricultural biodiversity. The problem of the industrial utilization of food plant oils has become more urgent with the development of the global biodiesel production. The remarkable advances made during the last decade in organic synthesis, catalysis, and biotechnology using plant oils and the basic oleochemicals derived from them will be reported, including, for example, \( \omega \)-functionalization of fatty acids containing internal double bonds, application of the olefin metathesis reaction, and de novo synthesis of fatty acids from abundantly available renewable carbon sources\(^1\).

Oleochemistry is the study of vegetable oils and animal oils and fats, and oleochemicals derived from these fats and oils or from petrochemical feedstocks through physico-chemical modifications or transformation.
Currently, it is represented as one of the major possibilities within the big challenge of chemistry of renewable products. First, it is used in the making of soaps, now it is part of our daily lives, where it is found in a wide variety of sectors like food industry, cosmetics industry, pharmaceutical industry, oleochemical industry and polymer industry².

Thus, before the advent of the modern food industry, vegetable oils (triglycerides) from many sources had a long history of use as condiments in cooking, personal care, and other therapeutic applications. Industrial applications of vegetable oils outside of food usage, on the other hand, have been limited on account of the shorter shelf-life durability of these oils resulting from the natural unsaturation in the structure of most triglycerides. In seeking, it is evident to explore the expanded utilization of this renewable resource³.

The production of unusual fatty acids in crop plants has been a long-standing goal of green chemistry. However, the expression of the enzymes that catalyze the primary synthesis of these unusual fatty acids in transgenic plants typically results in low levels of the desired unusual fatty acids⁴. Thus, the nature produces a wide variety of unusual fatty acids, some of which are important for industry and human health. The producing of the unusual fatty acids in agronomically suitable plants which has been a long-standing goal for companies and researchers involved in the field of oilseed engineering chemistry⁵-⁷. Amongst, the unusual fatty acids the most
important class is hydroxylated fatty acids, which accumulate up to 90% of total fatty acids in the seeds of castor (*Ricinus communis*). Such hydroxylated fatty acids are being explored in many industrial applications viz., polyesters, biodiesel, and lubricants.

Ricinoleic acid is the one of the most commercially available hydroxylated fatty acid, which has been found to be the most appropriate alternative for the synthesis of the fatty acid based polyanhydrides. Its advantage lies in bifunctionality due to a 12-hydroxyl group along with the acid group and, therefore, it can be incorporated into the polyanhydride backbone by the formation of an ester bond. Thus, polyanhydride synthesized from ricinoleic acid maleate or succinate and sebacic acid demonstrated the hydrophobicity, flexibility, biocompatibility and biodegradability.

The estolides are vegetable oil-based lubricants obtained from oleic acid or any source of hydroxy fatty acids. Therefore, such estolides are class of polyesters based on vegetable oils that are formed when the carboxylic acid functionality of one fatty acid reacts at the site of unsaturation of another fatty acid or by covalent ester bonds between hydroxyl moiety of one hydroxyl acid and the carboxyl moiety of another hydroxyl acid molecule. These compounds have a variety of potential applications as greases, plastics, inks, cosmetics, viscosity controller for chocolate, emulsifier in margarine and lubricants. As lubricants, the estolides have
been developed in order to overcome deficiencies associated with some characteristics of vegetable oils, which are known to have poor thermal oxidative stability, low hydrolytic stability and poor low temperature properties\textsuperscript{14}. These vegetable oil-based lubricants and derivatives have excellent lubricity and biodegradability properties and currently out-perform the commercially available industrial products such as petroleum-based hydraulic fluids, soy-based fluids, and petroleum oils\textsuperscript{14,15}.

Olefin metathesis is one of the very few fundamentally novel organic reactions discovered in the last 40 years. Among others, it opens up new industrial routes to important petrochemicals, polymers, oleochemicals and specialty chemicals. The most important applications of olefin metathesis in the field of petrochemicals are the olefins conversion technology process (originally the Phillips triolefin process) and the Shell higher olefins process\textsuperscript{16}.

Thus, the metathesis is an attractive reaction for the conversion of oleochemical feedstocks into useful chemical products. Thus, metathesis of unsaturated fatty acid esters (the oleochemical raw materials) provides a convenient route to unsaturated diesters which can be used as intermediates for the production of polymers and specialty chemicals. Cross-metathesis with olefins is a means to change the chain length of fatty acids and derivatives; cross-metathesis with ethane (\textit{ethenolysis}) gives compounds with terminal double bonds, having a broad range of applications.
Ethenolysis of fatty oils or triglycerides allows the transformation of long-chain fatty acid triglycerides into fatty oils of lower molecular weight. Several highly selective catalyst systems - homogeneous as well as heterogeneous - have proven to be successful for the metathesis of unsaturated esters. Especially modified heterogeneous rhenium and molybdenum based catalysts have attracted much attention.
References


