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## Epoxidation of Vegetable Oils and Fatty Acids: Catalysts, Methods and Advantages

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**Abstract:** This study has attempted to show the efficiency of epoxidation under different catalysts conditions. It was found that different catalysts have been used for epoxidation of oil and unsaturated fatty acid with almost complete conversion and mono-epoxide of unsaturated carbon. Catalysts such as  $H_2SO_4$ , Ti(IV)-grafted silica catalysts, tungsten-based catalyst, acidic ion, exchange resin, potassium peroxomonosulfate, alumina-catalyzed have been studied.  $H_2SO_4$  was found to be more effective in terms of oxirane complete conversion. The epoxidation of oils and unsaturated fatty acids is widely used for the production of oxiranes, valuable industrial products providing an access to various fine chemicals but none has yet found industrial application. The application of different catalysts enables the preparation of a number of epoxy compounds impossible to obtain by other methods, or considerable improvement of the yields of those currently studied.

**Key words:** Epoxidation, fatty acids, catalysts, vegetable oils

### INTRODUCTION

Vegetable oils are part of a larger family of chemical compounds known as fats or lipids. They are made up predominantly of triesters of glycerol with fatty acids and commonly are called triglycerides. Lipids are widely distributed in nature; they are derived from vegetable, animal and marine sources and often are by-products in the production of vegetable proteins or fibers and animal and marine proteins. Fats of all types have been used throughout the ages as foods, fuels, lubricants and starting materials for other chemicals. This wide utility results from the unique chemical structures and physical properties of fats. The chemical structures of lipids are very complex owing to the combination and permutations of fatty acids that can be esterified at the three (enzymatically non-equivalent) hydroxyl groups of glycerol. A generalized triglyceride has the structure shown in Fig. 1 (Wallace, 1978).

Many naturally occurring fats are made up of fatty acids with chain length greater than 12 carbon atoms; the vast majority of vegetable and animal fats are made up of fatty acid molecules of more than 16 carbon atoms. Marine fats are characterized by their content of larger-chain (up to  $C_{24}$ ) fatty acids. Thus, because the fatty acid portions of the triglycerides make up the larger proportion (ca 90% fatty acids to 10% glycerol) of the fat molecules, most of the chemical and physical properties result from the effects of the various fatty acids esterified with glycerol (Wallace, 1978).

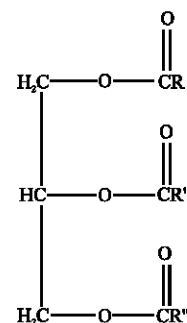


Fig. 1: General structure of a triglyceride

Non-edible oils uses depend mainly on the properties of the various fatty acids and fats although, some triglycerides are directly used as specialized lubricants. The many derivatives of fatty acids manufactures are used in surface coatings, plastics, detergents, lubricants, etc, where the long hydrocarbon chain confer needed plasticity, surface activity, or lubricity. In some instances, eg, drying oils, the reactive unsaturation of certain fatty acids is exploited and by means of catalyzed, oxidative polymerization, tough, flexible surface coatings are developed (Wallace, 1978).

The industrial chemistry of oils and fats is a mature technology, with decades of experience and refinement behind current practices. Environmental pressures demand cleaner processes and there is a market for new products. Current developments are in three areas: green chemistry, using cleaner processes, less energy and

renewable resources; enzyme catalyzed reactions, used both as environmentally friendly processes and to produce tailor-made products and novel chemistry to functionalize the carbon chain, leading to new compounds. Changing perceptions of what is nutritionally desirable in fat-based products also drives changing technology; interesterification is more widely used and may replace partial hydrogenation in the formulation of some modified fats.

The coverage in this study is necessarily selective, focusing on aspects of fatty acid and lipid chemistry relevant to the epoxidation and industrial exploitation of oils and fatty acids. The emphasis is on fatty acids and acylglycerols found in commodity oils and the reactions used in the food and oleochemical industries. Current areas of research, either to improve existing processes or to develop new ones, are also covered, a common theme being the use of chemical and enzyme catalysts.

Compounds of second-row transition metals rhodium and ruthenium and the oxides of rhenium and tungsten have attracted particular interest as catalysts for diverse reactions at double bonds. Recent interest in developing novel compounds by functionalizing the fatty acid chain is also mentioned. To date, few of these developments have found industrial use, but they suggest where future developments are likely. A number of recent studies and books cover and expand on topics discussed here (Akoh and Min, 2002; Gunstone and Hamilton, 2001; Gunstone and Padley, 1997; Gunstone, 1996).

## FATTY ACIDS

The number of triglycerides in a given natural fat is a function of the number of fatty acids present and the specificity of the enzyme system involved in the particular fat synthesis reaction. Litchfield (1972) points out that many plant seed fats have the potential to provide 125-1,000 different triglycerides, animal fats contain potentially 1000-64000 triglycerides species and butter fat could generate 2863288 triglycerides from 142 different fatty acids.

Most of the fatty acids in fats are esterified with glycerol to form glycerides. However, in some fats, particularly where abuse of the raw materials has occurred leading to enzymatic activity, considerable (>5%) free fatty acid is found. Hydrolysis occurs in the presence of moisture. This reaction is catalyzed by some enzymes, acids, bases and heat. Most producers of fats attempt to prevent the formation of free acids because certain penalties are assessed if they are present in the trading of crude and refined fats. As in the case of triglycerides, the number of known fatty acids is very large. Ca 900 vegetable and 500 animal fats have been analyzed Table 1 lists fatty acid prevalent in fats with their principal natural source and technical designation (Wallace, 1978).

Phospholipids (Fig. 2) occur in most natural fats with different amounts and compositions depending on the source of the fat. Owing to their complexity, these fat-soluble, biologically important compounds also have presented some intriguing analytical problems to chemists

Table 1: Representative fatty acids

Fatty acids	Common name (designation) <sup>a</sup>	Source
Butanoic	Butyric (4 :0)	Butter
Hexanoic	Caproic (6 :0)	Butter
Octanoic	Caprylic (8 :0)	Coconut
Decanoic	Capric (10 :0)	Coconut
Dodecanoic	Lauric (12 :0)	Coconut, palm kernel
Tetradecanoic	Myristic (14 :0)	Coconut, palm kernel, butter
Hexadecanoic	Palmitic (16 :0)	Palm, cotton, butter, animal and arine fat
cis-9-hexadecenoic	Palmitoleic (16 :1)	Butter, animal fat
Octadecanoic	Stearic (18 :0)	Butter, animal fat
cis-9-octadecenoic	Oleic (18 :1 9c)	Olive, tall, peanut, canbra, butter, animal and marine fat
cis,cis-9,12-octadecadienoic	Linoleic (18 :2 9c,12c)	Safflower, sunflower, com, soy, cotton
cis,cis,cis-9,12,15-octadecatrienoic	Linolenic (18 :3 9c,12c,15c)	Linseed
cis,cis,cis,cis-6,9,12,15-octadecatetraenoic	(18 :4 6c,9c,12c,15c)	Marine fat
cis, trans, trans-9,11,13-octadecatrienoic	α-oleostearic (18 :3 9c,11t,13t)	Tung
12-hydroxy-cis-9-octadecenoic	Ricinolenic (18:1 9c, 12-OH)	Castor
cis-9-eicosenoic	Gadoleic (20:1 9c) (20:1 11c)	Marine fat
cis-11-eicosenoic	Arachidonic	Rapeseed
all cis-5,8,11,14-eicosatetraenoic	(20:4 5c,8c,11c,14c)	Animal, marine fats
all cis-5,8,11,14,17-eicosapentaenoic	(20:5 5c,8c,11c,14c,17c)	Marine fat
Docosanoic	Behenic (22:0)	
cis-11-docosenoic	Cetoleic (22:1 11c)	Marine fat
cis-13-docosenoic	Erucic (22:1 13c)	Rapeseed

<sup>a</sup>No. or carbon atoms:number of unsaturation

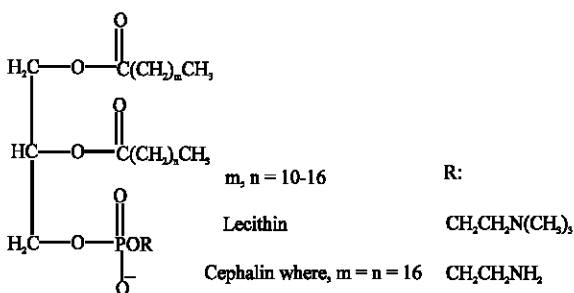


Fig. 2: Structure of phospholipids

and biochemists. From a technical standpoint, phospholipids, eg, from soybean, are composed mainly of lecithin, cephalin (phosphatidylethanolamine) or phosphatidylinositol. These complex mixtures (2-3% in soybean oil) are hydrated during the degumming step, removed and dried. These products are sold as commercial lecithin used in margarines, confections and shortenings where a fat-soluble emulsifier is required.

Sterols are of minor importance in the technology of fats. Normally they are removed in the refining and deodorization steps. The gross mixtures recovered from these processes have been utilized as source of certain phytosterols that are used as raw materials in the pharmaceutical industry (Seher *et al.*, 1976).

In addition to the materials of waxes, hydrocarbons, ketones, aldehydes and mono- and diglycerides are found in fats at varying but low levels. The waxes in some seed oils are troublesome and are removed to prevent haze formation in the finish product. The ketones and aldehydes probably arise from oxidative damage and can cause flavor and odors in fats. The mono- and diglycerides result from hydrolytic reactions either in the raw materials or during processing but do not pose particular problems in the end products. The hydrocarbons are mainly analytical curiosities.

### EPOXIDATION

Epoxides are produced by reaction of double bonds with peracids (Fig. 3a, b). This proceeds by a concerted mechanism, giving cis stereospecific addition. Thus, a cis olefin leads to a cis epoxide and a trans olefin to a trans epoxide. The order of reactivity of some peracids is m-chloroperbenzoic > performic > perbenzoic > peracetic; electron withdrawing groups promote the reaction. 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. Small scale reactions are carried out with

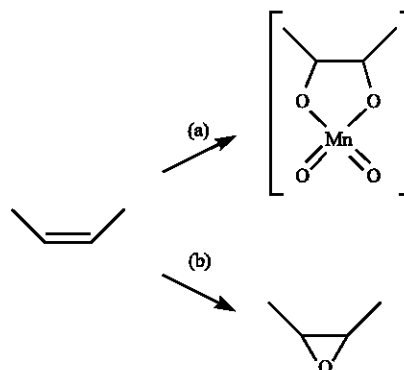


Fig. 3: Stereochemistry of epoxidation reactions with (a)  $\text{KMnO}_4$ , (b) m-chloroperbenzoic acid catalyzed hydrolysis

m-chloroperbenzoic acid in a halocarbon or aromatic solvent, in the presence of bicarbonate to neutralize the carboxylic acid as it is formed (Karlson *et al.*, 1994). Many studies have indicated the importance of using catalysts for epoxidation purposes.

**Acid catalysts:** The epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide has been studied by Goud *et al.* (2006). Mahua oil (*Madhumica indica*) was epoxidised *in situ* with hydrogen peroxide as oxygen donor and glacial acetic acid as active oxygen carrier in presence of catalytic amount of an inorganic acid. Catalytic loading of two different acids, i.e.,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were studied and  $\text{H}_2\text{SO}_4$  was found to be more effective in terms of conversion to oxirane. The effects of these parameters on the conversion to the epoxidised oil were studied and the optimum conditions were established. Relative conversion data showed that it was possible to develop epoxides from locally available natural renewable resources such as mahua oil. The epoxidation of MO using *in situ* generated peracetic acid could be carried out at moderate temperature range of 55-65°C. Higher temperatures and higher sulphuric acid concentrations reduced reaction time and resulted in higher oxirane content with lesser cleavage to glycol.  $\text{H}_2\text{SO}_4$  was found to be more effective in terms of oxirane conversion. The epoxidation reaction of mahua oil fell into kinetically controlled regime at stirring speeds >1500 rev/min. From the relative conversion data obtained for various reaction parameters, it could be concluded that it was possible to develop value added products such as epoxides from MO.

The kinetics of epoxidation of cottonseed oil by peroxyacetic acid generated *in situ* from hydrogen peroxide and glacial acetic acid in the presence of liquid inorganic acid catalysts were studied by Dinda *et al.*

(2008). It was possible to obtain up to 78% relative conversion to oxirane with very less oxirane cleavage by *in situ* technique. The order of effectiveness of catalysts was found to be sulphuric acid > phosphoric acid > nitric acid > hydrochloric acid. Acetic acid was found to be superior to formic acid for the *in situ* cottonseed oil epoxidation. The epoxidation of cottonseed oil using *in situ* generated peroxyacid could be carried out at moderate temperature of about 60°C. CH<sub>3</sub>COOH was found to be more effective oxygen carrier than HCOOH, in the present work. Out of all the liquid inorganic acid catalysts studied, H<sub>2</sub>SO<sub>4</sub> was found to be the most efficient and effective. Higher temperature and higher acid concentrations reduced the reaction time needed to reach the maximum conversion to oxirane value; however, it simultaneously increased the extent of oxirane ring cleavage to glycols. The reaction was kinetically controlled beyond a stirring speed of about 1800 rev/min. Maximum yield of oxirane with negligible amount of oxirane cleavage could be obtained if the epoxidation of cottonseed oil, using *in situ* generated peroxyacetic acid, is carried out at optimum conditions. These optimum conditions include a temperature range of 50-60°C, H<sub>2</sub>O<sub>2</sub>-to-unsaturation mole ratio range 1.5-2.0, CH<sub>3</sub>COOH-to-unsaturation mole ratio of about 0.5 and H<sub>2</sub>SO<sub>4</sub> loading of about 2% (by weight) of the aqueous phase.

Improved low temperature properties of 2-ethylhexyl 9(10)-Hydroxy-10(9)-Acyloxystearate Derivatives has been done by Salimon and Salih (2009a-d) The epoxidation of oleic acid and other unsaturated hydrocarbon chains using H<sub>2</sub>SO<sub>4</sub> as catalyst constitutes one of the most useful reactions in organic synthesis. As the epoxide group is an active intermediate, it can be readily transformed to the required functionality. Here, we report the synthesis of seven useful branched 2-ethylhexyl  $\alpha$ -hydroxy stearate esters from commercially available oleic acid and common organic acids. The common organic acids used here in were octanoic, nananoic, lauric, myristic, palmitic, stearic and behenic acids. One of the products, the behenic ester of 2-ethylhexyl hydroxy stearate showed to have pour point, flash point and viscosity indices of -53, 161°C and 215 cp, respectively, which is favourable properties in the synthesis of a bio-based lubrication base fluid. Overall, the epoxidation of oleic acid using H<sub>2</sub>SO<sub>4</sub> as catalyst was successfully proceed and the data indicated that most of these synthesized derivative compounds have significant potential as lubricant base oil.

The impact of the relevant process variables on the reaction of soybean oil fatty acid methyl esters with performic acid (PFA) generated *in situ* using concentrated

hydrogen peroxide (up to 60 wt.%), to produce an epoxidized product in high yield, is studied in detail (Campanella *et al.*, 2008). The degree of mixing, temperature, concentration and molar ratios of reactants and/or use of a diluents were considered. Temperature increases are significantly detrimental for achieving high oxirane numbers, as the selectivity to ring-opening reactions increases. Higher concentrations of either formic acid or H<sub>2</sub>O<sub>2</sub> are also harmful (particularly, the carboxylic acid) but much less than temperature. A proposed alternative process, employing moderate temperature (up to 40°C) and concentrated H<sub>2</sub>O<sub>2</sub>, compares favorably with the conventional one; higher conversion combined with high epoxide productivity and selectivity are attainable. Using economically sound reactants molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are well dispersed, the epoxidation process can be adequately described using an (equilibrated) two-phase reaction model. The model accounts for both the reversible per acid formation (in the aqueous phase) and the epoxidation reaction proper, together with the attacks on the epoxide ring by formic acid and performic acid (in the organic phase). In the epoxidation of soybean fatty acid methyl esters with PFA generated *in situ* from FA using highly concentrated hydrogen peroxide (up to 60 wt.%) and moderate temperature (preferably 40°C), the impact of temperature increases is significantly detrimental for achieving high yields and/or high oxirane-number. Higher concentrations of either formic acid or hydrogen peroxide are also harmful (particularly, the carboxylic acid) but much less than temperature. Nevertheless, this process alternative compares favorably to the conventional one, which is conducted at 60°C using 30 wt.% H<sub>2</sub>O<sub>2</sub>; higher double bond conversion combined with high epoxide productivity and excellent selectivity are attainable. Using economically sound FA-to-double bonds and H<sub>2</sub>O<sub>2</sub>-todouble bonds molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are always well dispersed, the epoxidation process can be adequately described using an (equilibrated) two-phase reaction model accounting for just the reversible per acid formation (in the aqueous phase) and the epoxidation reaction proper, together with the attacks on the epoxide ring by FA and PFA (in the organic phase).

The rate constants of epoxidation were determined by reacting formic acid with a number of oils, pure TAG and pure FAME (Scala and Wool, 2002). These results showed that FA composition had a significant effect on the value of the rate constant. In TAG, 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 unsaturation increased. Furthermore, the rate constants of epoxidation for the FAME were higher than their respective TAG. We conclude that steric and electronic effects caused FA with different levels of unsaturation to have different reactivities. These results were used to derive a model that predicts the epoxidation kinetics of oils from their FA composition. The predictions of the model closely match the experimentally determined rate constants.

The kinetics epoxidation of Rubber Seed Oil (RSO) by peroxyacetic acid generated *in situ* were studied at various temperatures (Okieimen *et al.*, 2002). It was found that epoxidation with almost complete conversion of unsaturated carbon and negligible oxirane cleavage can be attained by the *in situ* technique. The rate constant for epoxidation of RSO was found to be of the order of  $10^{-6}$  L/mol/sec and activation energy of epoxidation of 15.7 kcal mol<sup>-1</sup> was determined. Some thermodynamic parameters: enthalpy, entropy and free energy activation of 15.2, -31.94 and 25.44 kcal mol<sup>-1</sup>, respectively were obtained for the epoxidation of RSO. The results from this study show that the epoxidation of RSO by peroxyacetic acid generated *in situ* can be carried out at moderate temperatures with minimum epoxide degradation. The kinetic and thermodynamic parameters of epoxidation obtained from this study indicate that an increase in the process temperature would increase the rate of epoxide formation.

**Enzymes:** Epoxy alkylstearates were synthesized by lipase catalysed esterification and perhydrolysis followed by epoxidation of oleic acid in a one-pot process (Orellana-Coca *et al.*, 2007). Immobilized *Candida antarctica* lipase (Novozym<sup>®</sup> 435) was used as the catalyst. The esterification reaction occurred relatively quickly and was followed by epoxidation of the alkyl ester and the remaining fatty acid. Higher degree of esterification was achieved with n-octanol, n-hexanol and n-butanol as compared to that with ethanol and iso-propanol. The rate and yield of epoxidation was enhanced with iso-propanol but was lowered with the other alcohols. The lipase suffered significant loss in activity during the reaction primarily due to hydrogen peroxide. The presence of alcohols, in particular ethanol, further contributed to the enzyme inactivation. The epoxidation reaction could be improved by step-wise addition of the lipase. The enzymatic approach for the synthesis of alkyl epoxystearates is a simpler and energy efficient alternative to the chemical process and the solvent-free conditions and good product yields further

result in savings in product separation processes. The main limitation, however, is the low stability of the lipase under the reaction conditions employed. Possibility to use anhydrous reaction conditions and to minimize the exposure of the enzyme to the peroxide would be beneficial for improving product yields and performance of the biocatalyst.

Unsaturated carboxylic acids are converted to percarboxylic acids catalyzed by an immobilized lipase from *Candida antarctica* (Novozym 435R) (Warwel and Klaas, 1995). These unsaturated percarboxylic acids are only intermediates and epoxidized themselves in good yields and almost without consecutive reactions. The mechanism of the oxygen-transfer is found to be predominantly intermolecular and the formation of the percarboxylic acids proceeds via two different catalytic reactions. The lipase is surprisingly stable under the reaction conditions; it is recovered and reused fifteen times to produce epoxy-stearic acid on a multi-gram scale.

The effect of reaction parameters on lipase-mediated chemo-enzymatic epoxidation of linoleic acid was investigated by Orellana-Coca *et al.* (2005). Hydrogen peroxide was found to have the most significant effect on the reaction rate and degree of epoxidation. Excess of hydrogen peroxide with respect to the amount of double bonds was necessary in order to yield total conversion within a short time period, as well as at temperatures above 50°C to compensate for hydrogen peroxide decomposition. However, prolonged incubation with high excess of hydrogen peroxide leads to the accumulation of peracids in the final product. The reaction rate increased also with increasing hydrogen peroxide concentration (between 10 and 50 wt. %); however, at the expense of enzyme inactivation. Linoleic acid was completely epoxidized when used at a concentration of 0.5-2 M in toluene at 30°C, while in a solvent-free medium, the reaction was not complete due to the formation of a solid or a highly viscous oily phase, creating mass transfer limitations. Increasing the temperature up to 60°C also improved the rate of epoxide formation.

The parameters affecting the lipase activity and operational lifetime during chemo-enzymatic epoxidation of fatty acids were investigated (Tornvall *et al.*, 2007). Immobilized *Candida antarctica* lipase B (Novozym<sup>®</sup> 435) was incubated in the presence of various reaction components (i.e., toluene, water, H<sub>2</sub>O<sub>2</sub>, oleic acid, perpalmitic acid and epoxystearic acid, respectively) at temperatures between 20 and 60°C followed by measurement of residual enzyme activity. Epoxystearic acid was shown to slightly inactivate the enzyme at 50°C, while oleic acid and perpalmitic acid did not. No

deactivation of the enzyme was observed in presence of toluene/water mixture within 48 h at 20-60°C. In the presence of 6-12 M hydrogen peroxide, the enzyme was rather stable at 20°C, while at 60°C the enzyme lost activity rapidly, with the rate of deactivation increasing with increasing hydrogen peroxide concentration. In the work presented here, the parameters found to be most crucial for the activity and hence operational stability of Novozym<sup>®</sup>435 in chemo-enzymatic epoxidation of fatty acids, are hydrogen peroxide at high concentrations, together with elevated temperatures. For epoxidation processes run at elevated temperatures, controlled addition of H<sub>2</sub>O<sub>2</sub> is hence important for enzyme stability, especially in the beginning before the formation of water is sufficient to dilute the added H<sub>2</sub>O<sub>2</sub>. Since, the reaction is exothermic, a large-scale process would probably be most efficient if a temperature program is used. Concurrently with improving the process design, development of a more stable biocatalyst preparation would be an alternative strategy.

Enzymes were found to have significant effect on the reaction rate and degree of epoxidation with good yields.

**Ti(IV)-grafted silica catalysts:** The liquid-phase epoxidation of mixtures of Fatty Acid Methyl Esters (FAMEs) over titanium-containing silica materials, using tertbutylhydroperoxide (TBHP) as oxidant, is here reported (Guidotti *et al.*, 2006). The mixtures were obtained from vegetable renewable source, i.e., from high-oleic sunflower oil, coriander oil, castor oil and soya-bean oil. The influence of the nature and the position of functional groups on the C-18 chain of the FAMEs was studied. Very high activity and selectivity were obtained in the epoxidation of castor and soya-bean oil methyl esters in a reaction medium free from organic acids. Ti-MCM-41 (an ordered mesoporous titanium-grafted silica) displayed in this case, for the first time, superior performances, from a synthetic point of view, with respect to non-ordered mesoporous titanosilicates. Titanium-grafted mesoporous silica materials showed to be suitable catalysts for the epoxidation of unsaturated FAME mixtures in a reaction medium that is completely free from organic acids. They are also versatile, as they have been used over a series of four FAME mixtures obtained from different vegetable sources exhibiting interesting performances. In particular, very high conversion and selectivity values were obtained with Ti-MCM-41 in the epoxidation of castor oil or soya-bean oil FAME mixtures. In such cases, the superior catalytic performances displayed by this ordered mesoporous titanosilicate with respect to the other non-ordered materials can be explained by the

concurrency of various favourable factors, such as the presence of large amounts of highly accessible and well defined Ti(IV) tetrahedral active sites and the peculiar environment around the Ti(IV) sites (i.e., the high density of silanols surrounding the Ti(IV) sites), which accounts for the enhanced formation of epoxidised species when highly polar moieties (for instance, hydroxy-group in methyl ricinoleate or an epoxy-ring in methyl monoepoxyoctadecenoate) are already present on the substrate molecules. However, interesting performances were also recorded over grafted non-ordered silicas and, over these materials, the titanium sites (considered singularly) showed remarkable turnover frequency values, even higher than those obtained over Ti-MCM-41.

**Tungsten-based catalyst:** A solvent-free, rather complete and selective *cis* epoxidation of Methyl Oleate (MO) using a tungsten containing catalyst called Tetrakis (Poli *et al.*, 2009). High epoxide yields have been obtained by adjusting the reaction parameters (reaction time, temperature, gas phase, oxidant molar ratio and concentration). The highest selectivities are the result of a synergetic effect of hydrogen peroxide and air (or oxygen) used as oxidizing agents that decreases the MO dimerization and then favour the complete conversion of MO into its epoxide. The use of the Tetrakis phosphotungstate catalyst leads to a rather complete and selective transformation of *cis* MO into *cis* epoxide under greener conditions than what was obtained in previous studies because it is performed with a stoichiometric amount of hydrogen peroxide, without solvent and at a lower temperature leading to a maximal H<sub>2</sub>O<sub>2</sub> efficiency. Such a high yield is the result of a synergetic effect of hydrogen peroxide and air (or oxygen) used as oxidizing agents at a rather low temperature (313 K). This really high yield is also probably due to the low MO dimerization under these conditions because of the catalyst saturation by oxygen and also because of the modification of the H<sub>2</sub>O<sub>2</sub> decomposition equilibrium. Finally, this epoxidation method can be extended to other unsaturated fatty compounds and crude vegetable oils.

**Transition metal complexes:** The epoxidation of methyl linoleate was examined using transition metal complexes as catalysts (Du *et al.*, 2004). With a catalytic amount of methyltrioxorhenium (4 mol%) and pyridine, methyl linoleate was completely epoxidized by aqueous H<sub>2</sub>O<sub>2</sub> within 4 h. Longer reaction times (6 h) were needed with 1 mol% catalyst loading. Manganese tetraphenylporphyrin chloride was found to catalyze the partial epoxidation of methyl linoleate. A monoepoxidized species was obtained as the major product (63%) after 20 h.

**Ion exchange resin:** Canola oil with an iodine value of 112/100 g and containing 60% oleic acid and 20% linoleic acid, was epoxidised using a peroxyacid generated *in situ* from hydrogen peroxide and a carboxylic acid (acetic or formic acid) in the presence of an Acidic Ion Exchange Resin (AIER), Amberlite IR 120H (Mungroo *et al.*, 2008). Acetic acid was found to be a better oxygen carrier than formic acid, as it produced about 10% more conversion of ethylenic unsaturation to oxirane than that produced by formic acid under otherwise identical conditions. A detailed process developmental study was then performed with the acetic acid/AIER combination. The parameters optimised were temperature (65°C), acetic acid to ethylenic unsaturation molar ratio (0.5), hydrogen peroxide to ethylenic unsaturation molar ratio (1.5) and AIER loading (22%). An iodine conversion of 88.4% and a relative conversion to oxirane of 90% were obtained at the optimum reaction conditions. The heterogeneous catalyst, AIER, was found to be reusable and exhibited a negligible loss in activity. The epoxidation of canola oil using peroxy-carboxylic acid generated *in situ* was carried out most effectively using the acetic acid-acidic ion exchange resin combination. The epoxidation process with minimum oxirane cleavage was, therefore, optimized using acetic acid and the Amberlite IR- 120H (AIER) catalyst system. It was found that the epoxidation reaction occurred optimally at a temperature of 65°C, an acetic acid to ethylenic unsaturation molar ratio of 0.5:1, a hydrogen peroxide to ethylenic unsaturation molar ratio of 1.5:1 and a catalyst (AIER) loading of 22 wt.% of total canola oil used. Under these optimum conditions, 90% conversion of ethylenic unsaturation to oxirane was obtained, with a similar conversion of iodine. The AIER catalyst was found to be reusable. The formation of the epoxide adduct of canola oil was confirmed by FTIR and <sup>1</sup>H NMR spectral analysis. From the relative conversion data obtained, it can be concluded that it is possible to develop value-added products, such as epoxide, from canola oil.

The kinetics of the epoxidation of soybean oil in bulk by peracetic acid formed *in situ*, in the presence of an ion exchange resin as the catalyst, was studied by Sinadinovic-Fiser *et al.* (2001). The proposed kinetic model takes into consideration two side reactions of the epoxy ring opening involving the formation of hydroxy acetate and hydroxyl groups as well as the reactions of the formation of the peracid and epoxy groups. The catalytic reaction of the peracetic acid formation was characterized by adsorption of only acetic acid and peracetic acid on the active catalyst sites and irreversible surface reaction was the overall rate-determining step. Kinetic parameters were estimated by fitting experimental data using the Marquardt method. Good agreement

between the calculated and experimental data indicated that the proposed kinetic model was correct. The effect of different reaction variables on epoxidation was also discussed. The conditions for obtaining optimal epoxide yield (91% conversion, 5.99% epoxide content in product) were found to be: 0.5 mole of glacial acetic acid and 1.1 mole of hydrogen peroxide (30% aqueous solution) per mole of ethylenic unsaturation, in the presence of 5 wt.% of the ion exchange resin at 75°C, over the reaction period of 8 h.

**Methyltrioxorhenium (VII) on nobia:** Soybean oils (oleic, linoleic and linolenic acids and their methyl esters) are epoxidized readily with Urea-Hydrogen Peroxide (UHP) when methyltrioxorhenium(VII) supported on nobia is used as the catalyst in chloroform. Simple alkenes are epoxidized by the same method (Bouh and Espenson, 2003). The epoxide and not a diol is produced.

And also has been used the methyltrioxorhenium (MTO)-CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> biphasic system for epoxidizing soybean oil (Gerbase *et al.*, 2002). The reactions were optimized (reactant ratio, time and temperature), which resulted in a better performance (higher conversion and selectivity) than those described in the literature. Total double bond conversion and 95% selectivity were obtained in 2 h at room temperature. Furthermore, it was possible to reach desired epoxidation degrees by changing the oxidant and MTO amounts. The rhenium-epoxidized soybean oil remained stable in the absence of stabilizers for up to 30 day when stored at mild conditions.

Methyltrioxorhenium (MTO) catalyses direct epoxidation by hydrogen peroxide. The reaction is carried out in pyridine, avoiding acidic conditions detrimental to high epoxide yield and uses less concentrated hydrogen peroxide (30%) than other methods. This method epoxidized soybean and metathesized soybean oil in high yield. The epoxidized metathesized oil was more stable to polymerization than that produced using *m*-chloroperbenzoic acid, presumably because it was free of acidic impurities. These and other novel approaches to epoxidation have recently been reviewed. None has yet found industrial application.

**Amorphous Ti.SiO<sub>2</sub>:** A study of the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide in dilute solution (6 wt.%) using an amorphous heterogeneous Ti/SiO<sub>2</sub> catalyst in the presence of tert-butyl alcohol has been studied by Campanella *et al.* (2004). The influence of some relevant process variables such as temperature and the hydrogen peroxide-to-double bond molar ratio on performance is examined. The highest yields of epoxidized olefins were obtained upon using a



H<sub>2</sub>O<sub>2</sub>: substrate molar ratio of 1.1: 1. Higher ratios than this were not effective for speeding up the reaction. Under the experimental conditions employed in this work, no degradation of the oxirane ring was observed.

**Alumina:** Two commercial aluminas and one produced by the sol-gel process were compared for the epoxidation of unsaturated fatty esters using anhydrous or aqueous hydrogen peroxide as oxidant and ethyl acetate as solvent (Sepulveda *et al.*, 2007). The aluminas show a good catalytic activity and excellent selectivity towards the epoxides. The sol-gel alumina was more efficient and when using aqueous hydrogen peroxide could be recycled several times. Alumina synthesized by the sol-gel method is shown to be an inexpensive and efficient catalyst in the epoxidation of methyl oleate and soybean oil methyl esters with aqueous hydrogen peroxide as oxidant. A conversion of 95% and selectivity >97% for the epoxide were obtained after 24 h without the use of any kind of homogeneous acid. After 4 cycles, a conversion of 87% was obtained. These results show that sol-gel alumina is an alternative catalyst for the epoxidation of vegetable oils.

## CONCLUSIONS

Recent studies have attempted to improve the efficiency of epoxidation under milder conditions that minimize the formation of byproducts. Chemo-enzymatic epoxidation uses the immobilized lipase from *Candida antarctica* (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.

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