



Catalyst for epoxidation of oils: a review

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General Note

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ABSTRACT

This review focused on the finding of the potential utility of epoxidized vegetable oil and developing newer means for its wide spread applications. Vegetable oil finds sustainable and renewable source of raw material. The unsaturation present in vegetable oils can be chemically modified to a value added product by a complicated reaction called 'epoxidation'. Due to the high reactivity of the oxirane ring epoxides can also act as a raw material for synthesis of variety of chemicals such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers and their demand is increasing day by day. Recent studies have attempted to improve the efficiency of epoxidation under milder conditions that minimize the formation of by product. unsaturated fatty acid can be converted into epoxy fatty acid by conventional epoxidation, catalytic acidic ion exchange resin, metal catalyst epoxidation or using chemo enzymatic epoxidation, Transition metal complexes, Chlorinated KU-2× 8 Cation Exchanger, Ti (IV)-grafted silica catalysts

Key words: Epoxidation, Oxirane Oxygen Content, metal catalyst, Enzyme, ion exchange

1. INTRODUCTION

Renewable raw materials are known to be environment-friendly, biodegradable, low cost and readily available (Blayo et al, 2001). The use of these material resources in many applications has attracted the attention of many researchers due to their potential to substitute petrochemical derivatives (Adhvaryu et al, 2002). Plant oils and animal fat belong to such renewable resources with many versatile applications. The world production of plant oil and animal fat rose from 58.04mil-lion tons in 1980 to 114.50million tons in 2000 (Basiron et al,2003). It is projected that the demand for fat and oil will outgrow the supply in the year 2010 (Basiron et al,2003). The development in organic chemistry, due to better and improved analytical equipment, has made it possible to perform a comprehensive examination of the chemical composition, the structure, and the properties of natural products like vegetable oils. Modification and application of improved consumer-based products has continuously evolved (Carracher et al, 1983). This steady increase in various applications of fat and oil has triggered a world expansion of planted areas for these crops (Carracher et al, 1983). Recently, cultivation by means of genetic engineering, to develop high-oleic acid soy-bean and rapeseed oil (Adhvaryu et al, 2002, Warwel et al, 2001) as well as new oil seeds, is continuously being investigated and developed to meet growing demands

2. OVERVIEW OF EPOXIDATION

Epoxidation occurs when a cyclic ether is formed at sites of ethylenic unsaturation (C=C) located along the Fatty acid chains by the addition of an oxygen atom. The bond angles are about 60°, making the ring highly strained and highly reactive (Mungroo et al, 2008). The presences of these 'high strain energy'

rings on the fatty acid chains promote cross linking when the epoxy resin is cured. The higher the amount of epoxy rings that are opened by the process, the more cross linking can occur, and the higher the quality of the resulting plastic (Goud et al, 2006). The method of epoxidising vegetable oil that has received the most attention in the literature is by reacting vegetable oil with peroxy carboxylic acid. The peroxy carboxylic acid donates the oxygen atom required to form the epoxy group and returns carboxylic acid to the bulk mixture. Peroxy carboxylic acid is formed *in situ* by the reaction of carboxylic acid and hydrogen peroxide in the presence of an acidic ion exchange resin (AIER) as a heterogeneous catalyst (Sinadinovic-Fiser et al, 2001, Mungroo et al, 2008, Goud et al, 2007, Campanella et al, 2007, Du et al 2004). The *in situ* method is used because high concentrations of peroxy carboxylic acids can be unstable and explosive. By forming the peroxy carboxylic acid in the presence of a well dispersed oil phase, its consumption in the epoxidation reaction prevents regions of high concentration from occurring.

Epoxidation of fatty acids is a reaction of a carbon – carbon double bond with active oxygen, which results in the addition of an oxygen atom, converting the original double bond into a three membered epoxides (oxirane) ring. In general, olefins can be epoxidized with various per-acids is a chemical reaction in which an oxygen atom is joined to an olefinically unsaturated molecule to form cyclic, three-membered ether. The products of epoxidation are known as oxirane compounds or epoxide. Epoxidation of vegetable oils is a commercially important reaction because the epoxides obtained from these renewable raw materials and from their alkyl esters, their trans esterification products, have applications in such materials as plasticizers and polymer stabilizers. Furthermore, these epoxides can be used as intermediates in the production of a variety of derivatives, because of the high reactivity of the strained epoxide ring.

3. ACID CATALYSTS

The epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide has been studied by Goud (2006). Mahua oil (*Madhumica indica*) was epoxidized *in situ* with hydrogen peroxide as oxygen donor and glacial acetic acid as active oxygen carrier in presence of catalytic amount of an in organic acid. Catalytic loading of two different acids, i.e., H₂SO₄ and HNO₃ were studied and H₂SO₄ was found to be more effective in terms of conversion to oxirane. The effects of these parameters on the conversion to the epoxidized 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. H₂SO₄ 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 in organic acid catalysts were studied by Dinda (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 peroxyacids could be carried out at moderate temperature of about 60°C. CH₃COOH was found to be more effective oxygen carrier than HCOOH, in the present work. Out of all the liquid inorganic acid catalysts studied, H₂SO₄ 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, H₂O₂-to-unsaturation mole ratio range 1.5–2.0, CH₃COOH-to-unsaturation mole ratio of about 0.5 and H₂SO₄ loading of about 2% (by weight) of the aqueous phase. Improved low temperature properties of 2-ethylhexyl 9(10)-Hydroxy-10(9)-Acyloxystearate Derivatives have been done by Salimon and Salih (2009) the epoxidation of oleic acid and other unsaturated hydrocarbon chains using H₂SO₄ 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, they have report the synthesis of seven useful branched 2-ethylhexyl α-hydroxy stearate esters from commercially available oleic acid and common organic acids. The common organic acids used herein were octanoic, nonanoic, 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 are favorable properties in the synthesis of a bio-based lubrication base fluid. Overall, the epoxidation of oleic acid using H₂SO₄ 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 per formic (PFA) generated *in situ* using concentrated hydrogen peroxide (up to 60 wt.%), to produce an epoxidized product in high yield, were studied in detail (Campanella et al, 2008). The various parameters such as degree of mixing, temperature, concentration and molar ratios of reactants and/or use of 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 H₂O₂ 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 H₂O₂, 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 per formic (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.% H₂O₂; higher double bond conversion combined with high epoxide productivity and excellent selectivity are attainable. Using economically sound FA-to-double bonds and H₂O₂-to-double bonds molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are always well dispersed, the epoxidation

Fatty Acid	Systematic Name	Formula \ Structure
Lauric	Dodecanoic	12:0 \ C12H24O2
Myristic	Tetradecanoic	14:0 \ C14H28O2
Palmitic	Hexadecanoic 2	18:0 \ C18H36O2
Stearic	Octadecanoic	16:0 \ C16H32O
Arachidic	Eicosanoic	20:0 \ C20H40O2
Behenic	Docosanoic	22:0 \ C22H44O2
Lignoceric	Teracosanoic	24:0 \ C24H48O2
Oleic	cis-9-octadecanoic	18:1 \ C18H34O2
Linoleic	cis-9,cis-12- octadecadienoic	18:2 \ C18H32O2
Linolenic	cis-9,cis-12,cis 15Octadecatrienoic	18:3 \ C18H30O2
Erucic	cis-13-Docosenoic	22:1 \ C22H42O2

Figure 1

Chemical Structure of Common Fatty Acid

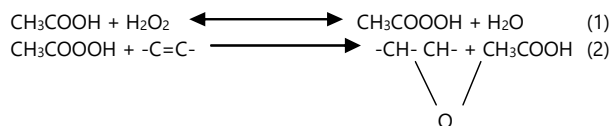


Figure 2

Proposed reaction of 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 triglycerides (TAG) and pure fatty acid methyl ester (FAME) (Scala et al, 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 fatty acid methyl ester were higher than their respective TAG. We conclude that steric and electronic effects caused fatty acid 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 [6]. 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 $15.7 \text{ kcal mol}^{-1}$ was determined. Some thermodynamic parameters: enthalpy, entropy and free energy activation of 15.2, -31.94 and $25.44 \text{ kcal mol}^{-1}$, 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.

4. ENZYMES

Epoxy alkylstearates were synthesized by lipase catalyzed esterification and per hydrolysis followed by epoxidation of oleic acid in a one-pot process (Orellana-Coca et al, 2007). Immobilized *Candida Antarctica* lipase (Novozym[®] 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 epoxy stearates 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 et al, 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 (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[®] 435) was incubated in the presence of various reaction components (i.e., toluene, water, H_2O_2 , 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 $20-60^\circ\text{C}$. 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[®] 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_2O_2 is hence important for enzyme stability, especially in the beginning before the formation of water is sufficient to dilute the added H_2O_2 . 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.

5. 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, was 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 were 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 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 titan silicates. 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 titan silicate with respect to the other non-ordered materials can be explained by the concurrence of various favorable 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 epoxidized species when highly polar moieties (for instance, hydroxy-group in methyl ricinoleate or an epoxy-ring in methyl mono epoxyoctadecenoate) 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.

6. 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, Mohamed Tahar et al, 2007). 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 favorable 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 H₂O₂ 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 H₂O₂ decomposition equilibrium. Finally, this epoxidation method can be extended to other unsaturated fatty compounds and crude vegetable oils.

7. TRANSITION METAL COMPLEXES

The epoxidation of methyl linoleate was examined using transition metal complexes as catalysts (3). With a catalytic amount of methyltrioxorhenium (4 mol%) and pyridine, methyl linoleate was completely epoxidized by aqueous H₂O₂ 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.

8. ION EXCHANGE RESIN

wild safflower oil (WSO) with an iodine value of 155(g I₂/100g), and containing 13% oleic acid (C 18:1) and 72% linoleic acid (C 18:2), was epoxidised using a peroxy acid generated *in situ* by the reaction of aqueous hydrogen peroxide and carboxylic acid in presence of strongly acidic Cation exchange resin, Amberlite® IR-122. (Pawan et al, 2011) Acetic acid was found to be a better oxygen carrier than formic acid and the use of catalyst improved the epoxide yield. A high temperature of above 60°C is detrimental since at continued reaction it accelerated the rapid destruction of oxirane rings. Higher concentrations of acetic acid and hydrogen peroxide (above 0.5 & 1.5 mol/mol of ethylenic unsaturation respectively) are also unfavourable as they lead to epoxy ring opening. The study shows that a relative conversion to epoxide ring moiety of 85% can be achieved by using the optimum molar ratio 1:0.5:1.5 (ethylenic unsaturation: acetic acid: hydrogen peroxide) at temperature 60°C and 2000rpm. The results of the present investigation shows that WSO can be successfully utilized for epoxidation using peroxy acid generated *in situ*. Acetic acid-IR-122 combination was found to be most effective for higher epoxide yield at shorter reaction time. The optimized parameters to get higher degree of epoxidation with minimum epoxy ring breaking were noted as temperature of 60°C, stirring speed 2000 rpm ensuring kinetically control of reaction, 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 (IR-122) loading of 20 wt% of WSO. Under these optimum conditions, 7.87% oxirane oxygen content in synthesized ESWO was obtained.

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 (26). 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 optimized 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 ¹H 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 in vegetable oil living 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.

9. METHYL TRIOXORHENIUM (VII) ON NOBIA

Soybean oils (oleic, linoleic and linolenic acids and their methyl esters) were epoxidized readily with Urea-Hydrogen Peroxide (UHP) when methyl trioxorhenium(VII) supported on nobia was used as the catalyst in chloroform. Simple alkenes are epoxidized by the same method. The epoxide and not a diol is produced. And also has been used the methyltrioxorhenium (MTO)-CH₂Cl₂/H₂O₂ biphasic system for epoxidizing soybean oil (4). 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) catalysed direct epoxidation by hydrogen peroxide. The reaction was 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.

10. AMORPHOUS Ti.SiO₂

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/SiO₂ catalyst in the presence of tert-butyl alcohol has been studied by (2). 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 H₂O₂: 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.

11. 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. (16) The aluminas showed 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 was 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 showed that sol-gel alumina is an alternative catalyst for the epoxidation of vegetable oils.

12. CHLORINATED KU-2× 8 CATION EXCHANGER

A study of the epoxidation of soybean oil in the Course of Cooxidation with Hydrogen Peroxide in the presence of propanoic Acid and Chlorinated KU-2×8 Cation Exchanger has been studied by (Gurbanov et al, 2005). The influence of some relevant process variables such as acetic acid and the hydrogen peroxide-to-double bond molar ratio on performance was examined. The catalyst. Some kinetic and activation parameters of soybean oil epoxidation were determined. The catalysts, chlorinated KU-28 Cation ex-changer with a 9.5 wt % chlorine content and a Chlorinated KU-2×8 Cation exchanger was highly active and stable catalyst for Soybean oil epoxidation in the presence of acetic acid & hydrogen peroxide. Chlorinated KU-2×8 Cation exchanger catalyzes only the formation of proxy propionic acid and has no effect on the rates of oxidation of the double bond of soybean oil and of the opening of the epoxy ring of the target product, which increases the selectivity and efficiency of epoxidation and improves the quality of the target product.

13. 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 per acids 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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