Microwave assisted epoxidation of soybean oil - An efficient method

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ABSTRACT

Epoxidized vegetable oil have creating much attention in recent years, especially in polymer industry as they are sustainable, renewable and biodegradable materials replacing petrochemical-based materials in some applications. In this study the Epoxidation of Soybean oil was carried out by using microwave irradiation and comparison was made with conventional heating. Effects of various reaction parameters such as power, mole ratio, catalyst, reaction temperature and time were investigated. The epoxidation of soybean oil using microwave rector was observed in terms of substantial reduction in the reaction time for similar levels of conversion by conventional heating. It was found that the relative percentage conversion to oxirane using the conventional method was about 85.5% in 8 h while using microwave rector, almost 83% conversion was obtained in 60 min. Also the effects of two different catalysts on epoxidation conversion were studied. It was found that, the conversion up to 97% was obtained by using Ion exchange resin as a catalyst by conventional method. FTIR analysis was used to identify the relative extent of epoxidation of the samples during the epoxidation reaction. The present work has clearly illustrated the microwave reactors for epoxidation reaction opening a new opportunity for commercial exploitation.

Keywords: *Epoxidation, Microwave heating, soybean oil, Epoxidized soybean oil, conversion efficiency.*

INTRODUCTION

In some past days several Scientists and Researcher reported the use of microwaves as an energy source for chemical reaction [1, 2, 3, 4]. Microwave irradiation is a well-known method for heating and drying materials and is applied in many private households and industrial applications for various purposes. It offers a number of advantages over conventional heating, such as noncontact heating, instantaneous and rapid heating and highly specific heating [5, 6].

Microwave assisted organic synthesis offered the shorter reaction times and expanded reaction range that are suited to the increased demands in industry. In general, most organic reactions have been heated using conventional heat transfer media such as oil baths, water bath, sand baths and heating jackets. These heating techniques develop a temperature gradient can develop within the sample and need more time to attained the desired temperature range and rather slow.

In fact, the development of microwave ovens for the heating of food has more than a 50-years history. In the 1970s the construction of the microwave generator, the magnetron, was both improved generator, the magnetron, was both improved and simplified. Consequently, the prices of domestic microwave ovens fell considerably, leading to them becoming a mass product. The design of the oven chamber or cavity, however, which is crucial for the heating characteristics, was not significantly improved until the end of the 1980s. In inorganic chemistry, microwave technology has been used since the late 1970s, while it has only been implemented in organic chemistry since the mid-1980s. Since the mid-1990s, however, the number of publications has increased significantly [6].

Soybean oil is a triglyceride that typically contains 14% stearic, 23% oleic, 55% linoleic, and 8% linolenic acid. Three of these are unsaturated acids: oleic (18:1), linoleic (18:2), and linolenic (18:3), structure are shown in Fig. 1,

Chemical modification of commercially available soybean oil, such as epoxidation, can enhance its properties (reactivity) for certain industrial applications. In a fully epoxidized soybean oil, the linolenic acid with three double bonds (positions 9, 12, and 15), is more reactive than linoleic, which contains two double bonds per molecule. Epoxidation of fatty acids is a reaction of a carbon–carbon double bond with an active oxygen, usually from a peroxide or a peracid, which results in the addition of an oxygen atom, converting the original –C=C– bond into a three-membered epoxide (oxirane) ring. The epoxidized soybean oil (ESO) is extensively used in the plastic industry as a plasticizer to increase flexibility in poly(vinyl chloride) (PVC) products and as a stabilizer to minimize their decomposition. Materials such as PVC and polystyrene frequently contain epoxidized oil at levels ranging from 0.1 to 27%. It is known that PVC undergoes decomposition with increasing temperature (dehydrochlorination). During the thermal decomposition, hydrogen chloride is eliminated from PVC, conjugated double bonds are formed, and the process is followed by a change in the polymer's coloration, which goes from yellow to orange, red, brown, and finally black. The epoxide ring from ESO reacts with hydrogen chloride generated by polymer degradation and restores the labile chlorine atoms back into the polymer's chains. This prevents PVC from further dehydrochlorination and preserves its color [7].

In order to follow the soybean oil epoxidation process, it is necessary to quantify three analytes related to the product's quality and process efficiency. The epoxide index (EI) is directly related to the stabilizer feature of the product: the higher the epoxide index, the more efficient will be the additive as a thermal stabilizer. The iodine index (II) is an indicator of the amount of unsaturation present in the epoxidized soybean oil, which is unknown a priori. The unsaturated bonds are halogenated and the reagent excess is quantified by iodometry. The water percentage resulting from washing of the nal product in the industrial process is another important analyte. Its concentration must be minimal, since water causes degradation of the epoxide group [8].

Looking for cleaner alternatives to classical syntheses, we have examined several protocols involving epoxidation reaction using microwave irradiation. More recently, several solid acid catalysts, including ion exchange resin employed in organic synthesis are found as efficient and reusable catalysts. We describe here the epoxidation of soybean oil by microwave assisted and conventional method to utilize it as a functional variant in polymer and coating application. Furthermore, a protocol for the microwave assisted synthesis route was developed and directly compared to the conventional heating route. In conventional heating synthesis microwave treatment oven has advantages over conventional heat treatment for example short reaction time.

MATERIALS AND METHODS

Materials
Soybean oil (refined) was obtained from *IPOL*, India. Glacial acetic acid obtained from *S.D fine chemicals limited* (Mumbai, India) and a 50% (w/w) solution of hydrogen peroxide from *S.D fine chemicals limited* (Mumbai, India) were used. *P*-toluene sulfonic acid was purchased from *S.D fine chemicals limited* (Mumbai, India) and sodium sulfate anhydrous from *Fisher Scientific*. Amberlite IR 120 was purchased from MERCK.

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Methods
Conventional Heating System set up
The epoxidation reaction was carried out in a 250 ml three neck flask equipped with stirrer, reflux condenser and thermocouple. The three neck flask was placed in a water bath. The optimal condition for epoxidation reaction of SBO using acetic acid was achieved at a reaction time of 8 hr and temperature of 60 ^{0}C with p-toluene sulfonic acid catalyst and hydrogen peroxide oxygen carrier. The following mole ratios of unsaturation, acetic acid and hydrogen peroxide were used; (1: 0.3/0.5/0.7: 1.5), (1: 0.5: 1/1.5/2) keeping other parameters constant (temperature, rpm, time). Effect of doubling the proportions of acetic acid and hydrogen peroxide to that of ethylenic unsaturation of SBO was examined. The ratio giving maximum oxirane conversion in minimum time was finalized. The reaction obtained with optimized ratio was carried out at different temperature (50^{0}C, 60^{0}C, 70^{0}C, 80^{0}C) at constant stirring speeds for 8hrs duration.

Microwave Heating System set up
The Microwave reactors used in the present work were MAS II Sineo microwave Technology Pvt. Ltd. We can varry the microwave power from 100 to 1000 W and tempreture upto 300°C. The epoxidation reaction was carried out in a 250 ml three neck flasks (nearly microwave transparent) equipped with magnetic stirrer, reflux condenser and addition dropping funnel. The three neck flask was kept inside the microwave reactor.

Experimental Reaction Procedure
Conventional Heating Reaction Procedure
A calculated amount of SBO was introduced in the reactor. A necessary amount of acetic acid (carboxylic acid to ethylenic unsaturation molar ratio, 0.5:1) and p-toluene sulfonic acid catalyst (1wt% of acetic acid and hydrogen peroxide) were added and heated with agitation for 15 min. Then necessary amount of 50% of aqueous hydrogen peroxide molar ratio of (1.5 mole of hydrogen peroxide per mole of ethylenic unsaturation) was then added dropwise into the mixture for 30 min with gradual increase in temperature to 60^{0}C. This feeding strategy was required to avoid overheating the system as the epoxidation reaction is highly exothermic. The reaction was well mixed and was performed at a stirring speed of 500 rpm under isothermal conditions at several temperatures and reaction times. The product of the reaction was next cooled and decanted for the separation of the organic-soluble compounds (epoxidized oil) from water soluble phase. The epoxidized oil was then washed with warm water (in small aliquots) to remove residual contaminants. The product was then analyzed to determine its iodine value and oxirane content.

Microwave Heating Reaction Procedure
Epoxidation was carried out in closed borosilicate (nearly microwave transparent) reaction vessels (250 mL capacity) in a microwave oven equipped with magnetic stirring and heated according to the temperature settings. The MW power input was optimized in order to study the effect of MW power on conversion of reaction. Zero time was taken as the desired operation mode was initiated. However the temperature has to be checked from time to time to ensure it has not exceeded its range. Hence, an Infrared thermometer was used to accurately check the temperature of the reaction mixture. Power settings were based on adjustments according to temperature of reaction needed. The mixture was reacted for 100- 120 minute cycles. The MW irradiation was interrupted for sampling, which took approx. 45 s from the instant the MW irradiation was interrupted to the instant the reaction temperature set point was reached causing a decrease in temperature of less than 1 °C.

The optimal condition for epoxidation reaction of SBO using acetic acid was achieved at a reaction time of 40-60 min and temperature of 60 ^{0}C with p-toluene sulfonic acid catalyst and hydrogen peroxide oxygen carrier. The following MW power were used; 300, 400, 500, 600 keeping other parameters constant (mole ratio, temperature, rpm, time). Effect of increasing the power on reaction conversion will be examined. The MW power giving maximum oxirane conversion in minimum time will be finalized.

ANALYTICAL TECHNIQUES AND CHARACTERIZATION
Iodine value
Iodine value of soybean oil before and after reaction was determined using standard Wij's method (AOCS Tg 1a-64) [9].

Acid value
The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. Acid values of all the samples were analyzed before and after epoxidation according to AOCS Method [10].

Saponification value
Each gram of oil containing more amount of triglycerol will require more amount of KOH and hence its saponification value will be higher. The saponification value is thus an indication of average molecular weight of the fatty acid in an triglyceride [11].

Oxirane Oxygen Content
The oxirane oxygen content was determined by using standard AOCS Cd 9-57 method. From the oxirane oxygen content values, the relative fractional conversion to oxirane was calculated from the following expression.

Relative conversion to oxirane = $\dfrac{OO_{exp}}{OO_{th}}$ (1)

Whereas OO_{exp} is the experimentally find value of oxirane oxygen content and OO_{th} theretical maximum oxirane oxygen in 100 gm oil, which was determined to be 6.89% from Eq. (2)

$$OO_{th} = \left\{ \frac{(IV_0 / 2A_i)}{[100 + (IV_0 / 2A_i)A_0]} \right\} \times A_o \times 100 \quad (2)$$

Where A_i (126.9) and A_o (16.0) are the atomic weights of iodine and oxygen, respectively and IV_o is the initial iodine value of the oil sample [12].

FTIR analysis
The synthesized samples along with raw material were analyzed using a Perkin-Elmer Spectrum One spectrometer. The transmission mode was used to obtain the IR of the samples. The scan range used was 4500 cm^{-1} to 500 cm^{-1}. The FTIR of Soybean oil (SBO) and Epoxidized Soybean oil (ESBO) was done for the confirmation of epoxy group formation in ESBO.

RESULTS AND DISCUSSION

The main objective of this work is to investigate the effect of the Microwave radiation on soybean oil during epoxidation process. The epoxidation of soybean oil was carried out by varying catalyst loading to investigate the influence of the catalyst effect. Furthermore, a protocol for the microwave assisted synthesis route was developed and directly compared to the conventional heating route. In our experiments the use of the microwave assisted route also showed a faster reaction time for synthesizing Epoxidized Soybean oil.

The raw oil was analyses first before epoxidation in order to calculate the mole ratio and compare the final product properties as shown in Table 1. All analyses are carried out by AOCS methods.

Epoxidation runs were conducted with the following range of variables: temperature, 50 to 80°C; hydrogen peroxide-to-ethylenic unsaturation ratio (mole per mole), 1 to 2; acetic acid-to-ethylenic unsaturation ratio (mole per mole), 0.3 to 0.7. The catalyst concentration was expressed as the percentage of "total weight of hydrogen peroxide and acetic acid added together". The epoxidation reaction was followed in each case by plotting relative fractional conversion to oxirane as a function of reaction time.

Microwave Assisted Epoxidation of Soybean oil
Effect of Mole Ratio on Conversion
Effect of acetic acid: oil (unsaturation) molar ratio on oxirane conversion.
(a) SBO: HCOOH: H$_2$O$_2$ → 1: 0.3: 1.5 & (b) SBO: HCOOH: H$_2$O$_2$ → 1: 0.5: 1.5 (c) SBO: HCOOH: H$_2$O$_2$ → 1: 0.7: 1.5

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Acetic acid takes part in the overall reaction as a catalyst in the formation of oxirane rings and as a reactant in the hydrolysis of the oxirane rings. To attain the maximum oxirane oxygen content, an optimal level of the acid can be used where both the effects are balanced with respect to the amount of acid required in the formation of peroxyacetic acid. Fig. 2a shows the results obtained for the three levels studied (0.5, 1, and 1.5 moles per mole of ethylenic unsaturation). The most favorable results occurred at the 0.5 mole ratio. It was seen that increasing the acid concentration increases the oxirane conversion and a faster reaction rate was observed. From Fig.2a, higher oxirane conversion rate was observed with increased molar ratio of acetic acid used. The reaction conversion of 82% was achieved within 40 min when 0.5 moles acetic acid was used while 46% conversion was obtained after 40 min of reaction on using 0.3 mole of acetic acid. However, from the stability point of view of epoxy rings, the use of higher acid concentrations is of no significance as the excess acid promotes the hydrolysis of the epoxide, thereby decreasing its final yield as observed in case of 0.7 moles of acetic acid the oxirane content is lowest than other. Thus it can be concluded an acid to ethylenic unsaturation molar ratio of 0.5 is optimum, since it gives a moderately high rate of epoxidation and a negligible rate of ring opening.

Effect of hydrogen peroxide: oil (unsaturation) molar ratio on oxirane conversion.
(a) SBO: HCOOH: H_2O_2 → 1: 0.5: 1 & (c) SBO: HCOOH: H_2O_2 → 1: 0.5: 1.5   (c) SBO: HCOOH: H_2O_2 → 1: 0.5: 2

The effect of the hydrogen peroxide-to-ethylenic unsaturation mole ratio on relative fractional conversion to oxirane was studied in the ratio range of 1 to 2.The reaction rate increased as the concentration of hydrogen peroxide in the system increased (Fig. 2b). Although the maximum relative conversion to oxirane rate was attained for 2.0 moles per mole of ethylenic unsaturation, the stability of the oxirane ring was very poor (Fig. 2b). For higher H_2O_2 concentrations at the same temperature, the relative conversions to oxirane decreased more rapidly. In the experimental range explored, the optimal concentration appeared to be 1.5 moles of H_2O_2 per mole of ethylenic unsaturation. With an increase in the hydrogen peroxide to ethylenic unsaturation molar ratio twice as original ratio, there was an increase in the rate of oxirane formation. The reaction rate increased with an increase in concentration of H_2O_2 in the reaction. However; although the maximum conversion (82%) of double bonds to epoxide rings was achieved with 1.5 mole of H_2O_2 concentration after 40 min, it also tend to destroy the epoxy rings when reaction was continued further. Moreover, the epoxy rings formed for 1.5:1 mole ratio of H_2O_2 -to-ethylenic unsaturation shows excellent stability. Therefore, the optimal hydrogen peroxide-to-ethylenic unsaturation molar ratio was found to be 1.5:1 with a relative oxirane conversion of 82%.

Effect of time and power on Conversion
The effect of power and time on conversion showed in Fig 3. Effects of various reaction parameters such as power, mole ratio, catalyst ratio, reaction temperature and time were investigated. Oxirane content of Epoxidized soybean oil were determined by AOCS cd 9-57. Under optimized conditions, the iodine value of oil was reduced from 141 to almost 20 at temperature of 60^0C using the microwave reactor.

It was observed from the Fig 3 that as the Microwave power increases the epoxidation conversion up to the certain power, while at higher power the epoxidation conversion was lower due to the low stability of epoxides group. At higher power it was observed that the viscosity of product goes increases which are due to the side reaction of epoxy group or the chances formation of hydroxyl group was also more at higher power.

Effect of Type of catalyst on Conversion of Epoxidation of soya oil by Microwave Reactor
Acidic ion exchange resins (AIER) allow, in principle, the isolation of strong acid sites from the liquid mixture, together with their easy separation. In these *in situ* processes, three phases are simultaneously present in the reacting system: (a) an aqueous phase, immiscible with (b) the organic phase, and (c) the solid catalyst (which is hydrophilic). Hydrogen peroxide – an oxidant is made to react with acetic acid (AA) – an oxygen carrier – in the aqueous phase, to give peroxyacetic acid (PAA), inside the resin beads. Peroxyacetic acid attacks the double bonds of the unsaturated vegetable oil in the organic phase to form the oxirane ring, giving acetic acid as the co-product, which returns to the aqueous phase to close the sequence. In this study the epoxidation of Soybean oil with peroxyacetic acid formed *in situ* from acetic acid and hydrogen peroxide in the presence of AIER as the catalyst were carried out.

Fig 4 clearly shows the effect of different catalyst on conversion of epoxidation reaction. The oxirane oxygen content increased up to certain level and then decreased in case of p-TSA catalyst because of side reaction and oxirane opening but in case of AIER catalyst the side reaction are minimum hence the oxirane content is goes on increasing.

Effect of Catalyst loading on conversion of Epoxidation by Conventional and Microwave method
As the catalyst loading increase in reaction, the generation of actives site at same time will be also increases. An increase in the loading of a fixed-size catalyst leads to an increase in both the total active volume and the total surface area. The active species present on the surface might play an increased contributory role with the increase in optimum catalyst concentration. It was expected that an increase in the catalyst concentration would be associated with an increase in the rate of *in situ* peroxyacetic acid formation; the catalytic effect of the strongly acidic ion exchange resin on the epoxidation of soybean oil was investigated by using 5, 10, 15, and 20 wt% of Amberlite IR-120 by conventional Heating and Microwave heating. It was observed that an increase in the catalyst loading resulted in an increase in the oxirane oxygen formation. Since the maximum relative conversion to oxirane, obtained with 15% catalyst loading, was 17.0% lower than that achieved with 20% loading in microwave assisted system, the optimal quantity of the catalyst was selected to be 15%. Fig. 5a and 5b depicts the effect of the catalyst loading on the course of the epoxidation by both methods.

Conventional Epoxidation of Soybean oil
Effect of Mole ratio on Conversion
Effect of acetic acid: oil (unsaturation) molar ratio on oxirane and iodine conversion.
(a) SBO: HCOOH: H_2O_2 → 1: 0.3: 1.5 & (b) SBO: HCOOH: H_2O_2 → 1: 0.5: 1.5 (c) SBO: HCOOH: H_2O_2 → 1: 0.7: 1.5

The study on different acetic acid concentrations as an oxygen carrier was optimized from 0.3, 0.5, and 0.7 moles per moles of unsaturation for the conversion rate with respect to 1.5 moles hydrogen peroxide per mole of unsaturation. Optimal amount of acetic acid is required to accelerate the formation of oxirane rings with minimal oxirane ring cleavages. Increasing the amount of acetic acid leads to more production of peracetic acid. Fig. 6a indicates that the oxirane formation was increased and % conversion was decreased as the mole ratio of the acetic acid used was increased. The conversion of double bonds to epoxy rings achieved 85.5% at 0.5 moles of acetic acid per mole unsaturation. A 0.5 moles of acetic acid per mole of unsaturation was chosen because it balanced the effects of the oxirane ring formation and its destruction resulting in a stable maximum in oxirane content. Furthermore, using less acetic acid also resulted in cost-savings.

From Fig 6a, it was seen that increasing the acid concentration increases the oxirane conversion and a faster reaction rate was observed. From Fig.4.1, higher oxirane conversion rate was observed with increased molar ratio of acetic acid used. The reaction conversion of 65% was achieved within four hour when 0.7 mole acetic acid was used while 42% conversion was obtained after 4 hours of reaction on using 0.3 mole of acetic acid. However, from the stability point of view of epoxy rings, the use of higher acid concentrations is of no significance as the excess acid promotes the hydrolysis of the epoxide, thereby decreasing its final yield. Thus it can be concluded an acid to ethylenic unsaturation molar ratio of 0.5 is optimum, since it gives a moderately high rate of epoxidation and a negligible rate of ring opening.

Effect of hydrogen peroxide: oil (unsaturation) molar ratio on oxirane conversion.
(a) SBO: HCOOH: H_2O_2 → 1: 0.5: 1 & (c) SBO: HCOOH: H_2O_2 → 1: 0.5: 1.5   (c) SBO: HCOOH: H_2O_2 → 1: 0.5: 2

A series of reaction with different amount of Hydrogen peroxide was studied. The reaction showed that peracetic acid formed instantly upon the addition of hydrogen peroxide. The generated intermediate compound, peracetic acid, was reactive and unstable. Therefore, hydrogen peroxide was added dropwise to avoid excessive heat generation and to avoid the epoxy. Peracetic acid reacts with the double bond to formed oxirane rings. The oxirane oxygen content of the final product obtained from the system using 1.5 moles of hydrogen peroxide per mole of unsaturation was highest with 85.5% conversion.

The effect of the hydrogen peroxide-to-ethylenic unsaturation mole ratio on relative fractional conversion to oxirane was studied in the ratio range of 1 to 2. The reaction rate increased as the concentration of hydrogen peroxide in the system increased (Fig. 6b). Although the maximum relative conversion to oxirane was attained for 1.5 moles per mole of ethylenic unsaturation, the stability of the oxirane ring was very poor (Fig. 6b). However, little difference was observed in the final conversion attained for mole ratios of 1.5 and 2.0. For higher H_2O_2 concentrations at the same temperature, the relative conversions to oxirane decreased more rapidly. In the experimental range explored, the optimal concentration appeared to be 1.5 moles of H_2O_2 per mole of ethylenic unsaturation.

With an increase in the hydrogen peroxide to ethylenic unsaturation molar ratio twice as original ratio, there was an increase in the rate of oxirane formation. However, the reaction rate increased with an increase in concentration of H_2O_2 in the reaction. However; although the maximum conversion (85.5%) of double bonds to epoxide rings was achieved with 1.5 mole of H_2O_2 concentration after 6 hours, it also tend to destroy the epoxy rings when reaction was continued further. Moreover, the epoxy rings formed for 1.5:1 mole ratio of H_2O_2 -to-ethylenic unsaturation shows excellent stability. Therefore, the optimal hydrogen peroxide-to-ethylenic unsaturation molar ratio was found to be 1.5:1 with a relative oxirane conversion of 85.5%.
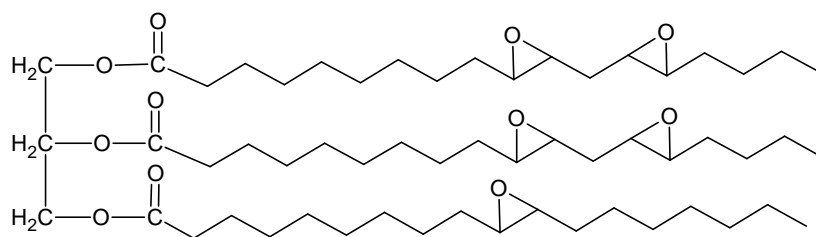
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Fig. 1   Structure of product: Epoxidized Soybean oil (ESBO)

Table 1. Analysis of Soybean Oil before Epoxidation

Sr. No	Analysis	Results
		SBO
1	Specific gravity@30^{0}C (AOCS To 1b-64)	0.916
2	Iodine Value (AOCS Tg 1a-64)	117 gm/100g Oil
3	Acid Value (AOCS Te 2a-64)	0.86 mg KOH/gm
4	Saponification Value (AOCS TI 1a-64)	180
5	Molecular Weight	952.89
6	Color (Gardner Scale) (AOCS Td 1a-64)	5
7	Viscosity@ 30^{0}C (cP) (Brookfield Viscometer)	80
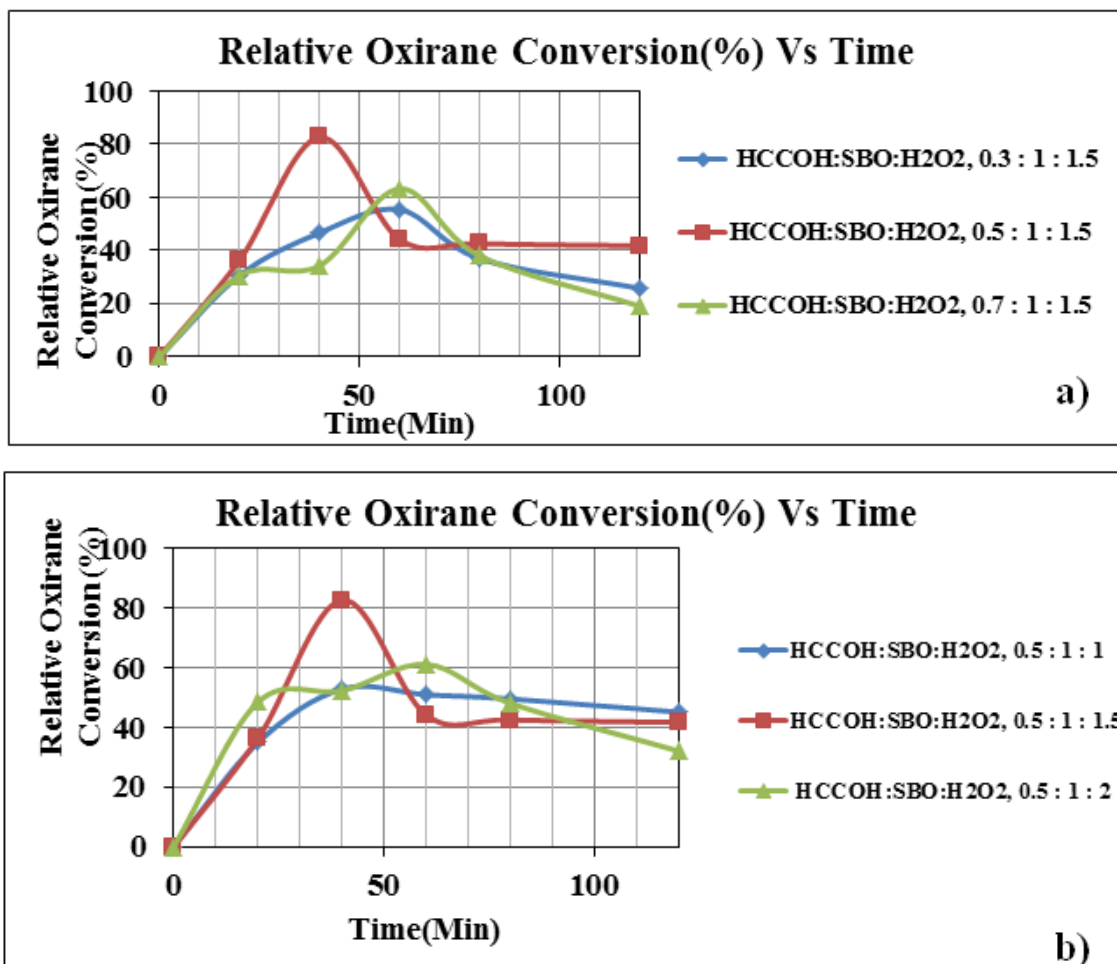
Fig. 2 (a) Effect of acetic acid per mole of ethylenic unsaturation on relative conversion (%) to oxirane. Conditions: SBO: HCOOH: H$_2$O$_2$=> (a) 1: 0.3: 1.5 (b) 1: 0.5: 1.5 (c) 1: 0.7: 1.5 ; P-TSA (1%); stirring speed, 500 rev/min; temperature, 60°C. (b) Effect of hydrogen peroxide per mole of ethylenic unsaturation on relative conversion (%) to oxirane. Conditions: SBO: HCOOH: H$_2$O$_2$=> (a) 1: 0.5: 1 (b) 1: 0.5: 1.5 (c) 1: 0.5: 2 ; P-TSA (1%); stirring speed, 500 rev/min; temperature, 60°C.
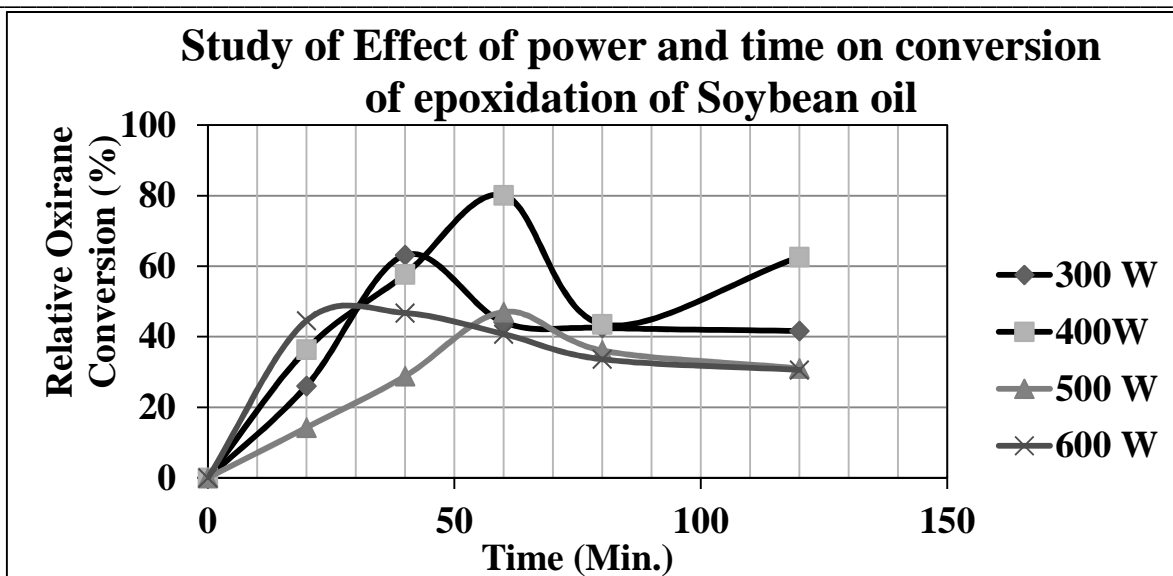
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Fig. 3 Effect of time and power on relative conversion (%) to oxirane. Conditions: SBO: HCOOH: H_2O_2 => 1: 0.5: 1.5; P-TSA (1%); stirring speed, 500 rev/min; temperature, 60°C; Power, 300, 400, 500, 600; Time, 0 to 120 Min.
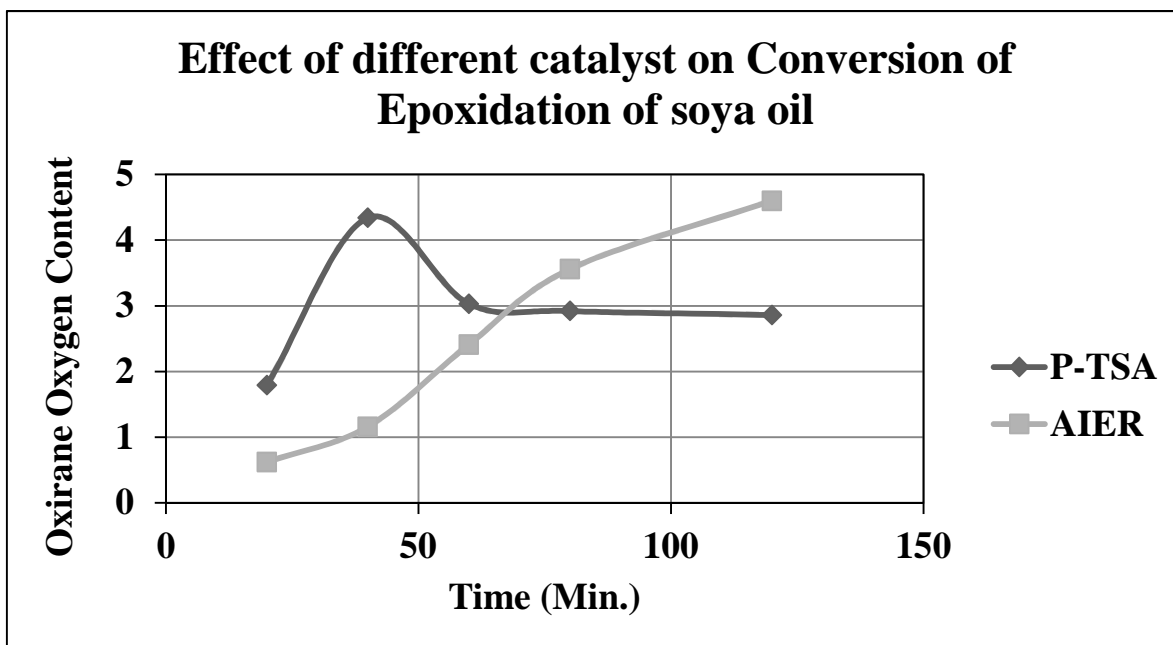

Fig: 4 Effect of different catalyst (P-TSA & AIER) on relative conversion (%) to oxirane. Conditions: SBO: HCOOH: H_2O_2 => 1: 0.5: 1.5; P-TSA (1%); AIER (15%); stirring speed, 500 rev/min; temperature, 60°C; Power, 300; Time, 0 to 120 Min.
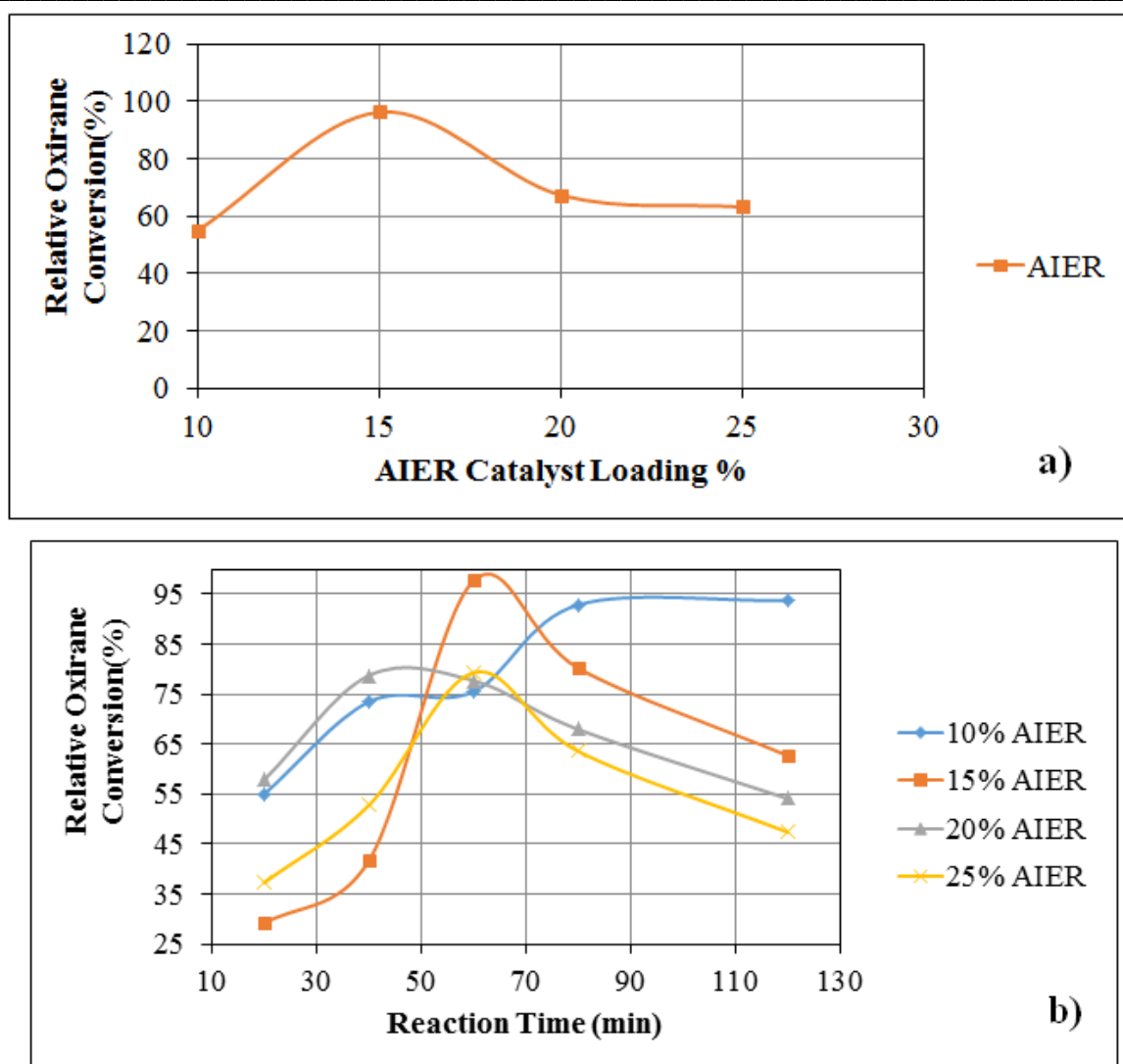
Fig: 5 (a) Effect of ion exchange resin (AIER) on relative conversion (%) to oxirane by conventional method. Conditions: SBO: HCOOH: H_2O_2 => 1: 0.5: 1.5; AIER (10%, 15%, 20%, 25%); stirring speed, 500 rev/min; temperature, 60°C; Time, 8 hr. (b) Effect of ion exchange resin (AIER) on relative conversion (%) to oxirane by Microwave method. Conditions: SBO: HCOOH: H_2O_2 => 1: 0.5: 1.5; AIER (10%, 15%, 20%, 25%); Power, 400 W; stirring speed, 500 rev/min; temperature, 60°C; Time, 0 to 120 Min.
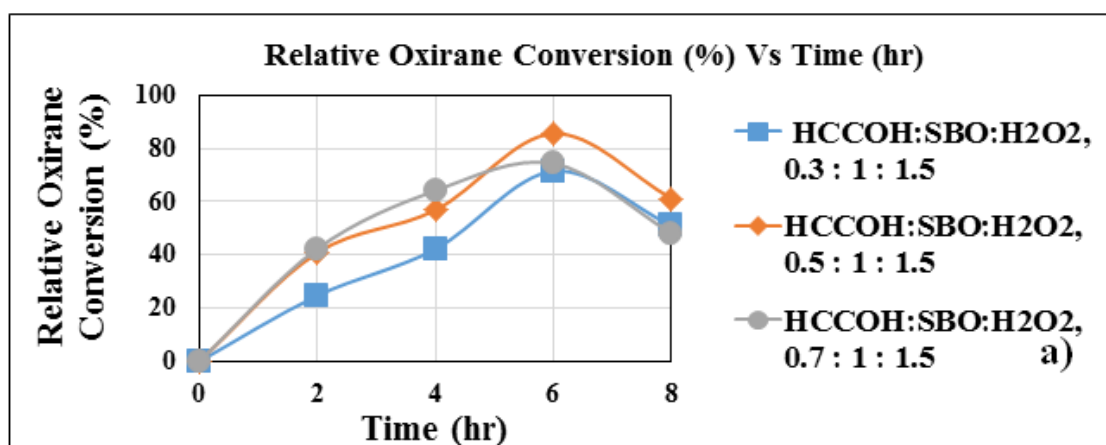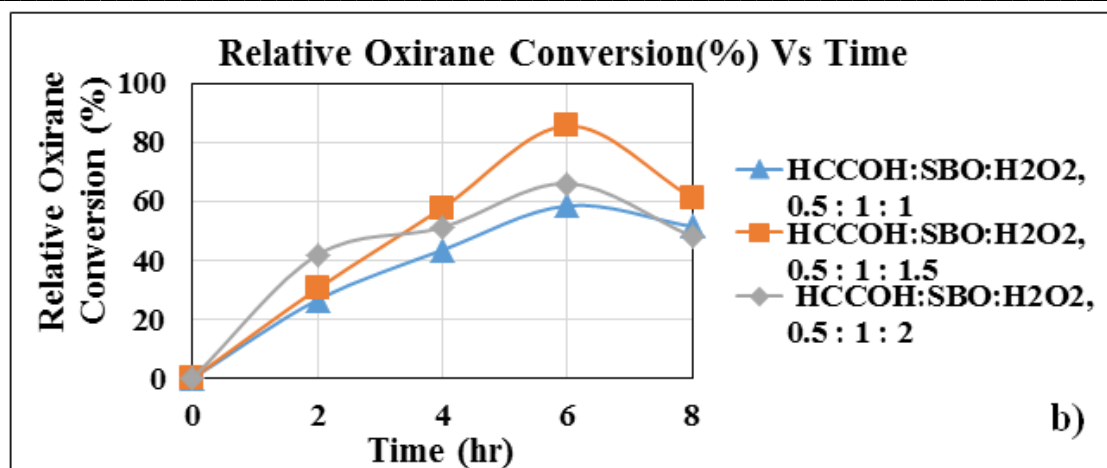
Fig. 6 (a) Effect of Acetic acid on relative conversion (%) to oxirane, Conditions: SBO: HCOOH: H_2O_2 => (a) 1: 0.3: 1.5 (b) 1: 0.5: 1.5 (c) 1: 0.7: 1.5 ; P-TSA (1%); stirring speed, 500 rev/min; temperature, 60°C; Time, 8 hr. (b) Effect of H_2O_2 on relative conversion (%) to oxirane, Conditions: SBO: HCOOH: H_2O_2 => (a) 1: 0.5: 1 (b) 1: 0.5: 1.5 (c) 1: 0.5: 2 ; P-TSA (1%); stirring speed, 500 rev/min; temperature, 60°C; Time, 8 hr.

Table 2. Optimized Result for ESBO synthesis

Sr. No	Test	Conventional Method- 60°C for 8hr-P-TSA. SBO:HCOOH:H_2O_2=>1:0.5:1.5	Microwave Method-60°C for 60 Min. at 400 W-P-TSA SBO:HCOOH:H_2O_2=>1:0.5:1.5
1	Specific gravity@30°C (AOCS To 1b-64)	0.98	0.96
2	Iodine Value (AOCS Tg 1a-64)	20	18
3	Acid Value (AOCS Te 2a-64)	3.9	3.3
4	Saponification Value (AOCS TI 1a-64)	192	201
5	Color (Gardner Scale) (AOCS Td 1a-64)	4	3
6	Viscosity@ 30°C (cP) (Brookfield Viscometer)	87	75
7	Oxirane Oxygen Content	5.8	5.68
8	% Conversion	84.17	82.43

FTIR

Epoxidized Soybean oil was characterized by FTIR (Fourier transform infrared spectrometry) shown in Fig.7, in order to monitor the disappearance of double bonds and formation of epoxy groups. The presence of new peaks in the FTIR spectrum of ESBO at 823.56 cm–1, attributed to the epoxy group, confirmed the success of the epoxidation reaction of SBO. The other new peak at the 3468.64 cm^{-1} was attributed to the hydroxyl functional group, derived from the epoxy functional group via partial epoxy ring opening reaction. The epoxy ring opening reaction could occur either by acid catalysis in the presence of water associated with aqueous solution of H_2O_2 used. The intensity of the peak indicates the extent of epoxidation of the samples.

The optimized result for conventionally and microwave assisted synthesize epoxidized soybean oil was shown in Table 2.

CONCLUSION

Controlled MW irradiations have significant effects in the ESBO ring openening reactions under solvent-free condition. Irradiating at intense MW powers namely, higher than 500 W, cause increase in ring opening of epoxy group which led significant decreanents in the epoxidation yields. Reaction products are easy to workup and the method is convinient simple and eco-friendly.

The effect of heating method like thermal heating and microwave heating on epoxidation conversion was studied. The effect of catalyst loading and the different type of catalyst on epoxidation conversion was also carried out. In the epoxidation reaction of SBO by conventional method, when molar ratio of SBO, acetic acid and hydrogen peroxide i.e. SBO: HCOOH: H_2O_2 was 1: 0.5: 1.5, oxirane content of 5.8% (84% conversion) and iodine value of 20 I_2/100g was observed at 60°C in 6 hrs reaction duration using P-TSA catalyst(1%). In the epoxidation reaction of SBO by Microwave method, when molar ratio of SBO, acetic acid and hydrogen peroxide i.e. SBO: HCOOH: H_2O_2 was 1: 0.5: 1.5, oxirane content of 5.68% (82% conversion) was observed at 60°C in 60 Min reaction duration using P-TSA catalyst(1%) which shows drastic reduction of reaction time as compared to conventional heating.

Also the conversion of SBO to ESBO up to 97% was obtained with help of Ion Exchange resin catalyst of 15% loading via a microwave assisted method and by conventional heating almost 96% conversion obtained for 15% loading of ion exchange resin catalyst.

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