

Mole Ratio of Eco-Friendly Epoxidation of Citrullus Lanatus (Watermelon) Seeds Oil

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Abstract

The mole ratio of epoxidation of Watermelon seed oil (*Citrus lanatus*) was studied in situ formed by the reaction of hydrogen peroxide and glacial acetic acid, acting as precursor of peroxy-acetic acid (behave as active oxygen carrier), in the presence of catalyst in inert solvent (maintain the stability of epoxidised product). Choice of catalyst (Amberlite IR-120) got priority as eco-friendly and more effective in terms of oxirane conversion instead of mineral acids i.e. H_2SO_4 and HNO_3 . The epoxidation of Watermelon seed (WMSO) oil was proceeded in two main reaction phases via Homogenous & Heterogeneous phase. In heterogeneous phase, reaction starts with the formation of initiator like peroxy-carboxylic acid by excitingly combination of hydrogen peroxide with carboxylic acids (liquid phase) using a catalyst (solid phase). This leads to next step, i.e. combination of peroxy-carboxylic acid (liquid phase) with unsaturated fatty acid (liquid phase) giving homogenous phase reaction. The relative epoxy yield was achieved at 333K (60°C) after 6 hrs when Amberlite IR-120 was taken as 3% of total weight of acetic acid and 30% aqueous H_2O_2 per mole of double bond in oil.

Keywords

In Situ Epoxidation, Watermelon Seed Oil (WMSO), Acidic ion Exchange Resin, Peroxy-Acetic Acid (PAA), Kinetics

1. Introduction

Watermelon (*Citrus Lanatus*) is a member of plant family cucurbitaceae, has physical appearance of green coloured large oval shaped fruit and may have colour range (Green to pale yellow) according to locality and ripening time, containing pulp and large number of seeds, found all over the world. It is grown in warmer & underground areas. It is enriched with bundles of vitamins, water content upto 92% of its weight [3] and carotenoids which act as antioxidants in metabolic reactions [1]. It is a tremendous fruit having each part beneficial for human life and can be used in different fields of research and have pharmacological benefits.

Watermelon seed oil is constituted on fatty acids; majorly unsaturated fatty acids in descending order such as linoleic acids (65%), oleic acid (23%), linolenic acid (8%) and less contribution of saturated fatty acid like stearic acid (14%) [2]. Concentration of fatty acids in seed oil depends upon oil

content in seed. it is calculated that 100g of seed yields 41.32% oil [3]. These fatty acids mainly constituted of C-18 skeleton with variation of degree of unsaturation. Linolenic acid has three time greater unsaturation (three double bonds) while linoleic acid has twice degree of unsaturation (two double bonds) than oleic acid. Due to this variation of unsaturation, multiple products are formed with different molecular masses. Unsaturation level can be confirmed by iodine no. or epoxidation level [4]. Epoxy resins are shortly named to the product as consisting of poly-epoxide based polymer. All epoxy resins have same backbone composition but potentially different from each other just due to having different sources of polyols which are synthesized from vegetable oil polyols [5]. The use of vegetable oil as a source has been the focusing point of researchers' interest from many years.

Vegetable oil is potentially used due to renewable resources and eco-friendly factor because of high bio-degradable rates than other mineral oils [6]. Therefore, it is largely being used in for the synthesis of diversified products like polyurethanes,

as a coating layer, lubricant and for insulation in transformer by its chemical modification. Oil is a basically class of naturally occurring organic compound that is lipid. Structurally lipids are consisted of fatty acids weighted as 90% and rest 10% weighted by polyols, i.e. glycerols [7]. Both these components make triester through condensation by releasing water molecule known as triglycerides.

Epoxidation is a process of elimination of unsaturation across C=C of fatty acids by addition of active oxygen atom to form epoxide, i.e. three-member heterocyclic ring. This active oxygen adds exceptional properties of oxirane group [8] so epoxidation of watermelon seed oil results in favourable alteration in structures of oleic acid, linoleic acid and linolenic acid while stearic acid remains unchanged owing to its saturated characteristic. Olefinic compounds can be epoxidized by following different mechanism such as epoxidation through conventional method, epoxidation through acidic ion exchange method, epoxidation through enzymatic activity and some other methods.

In conventional method, strong mineral acids like sulphuric acid or phosphoric acid can be used as inorganic catalyst. These may lead to problems like epoxide ring opening, corrode apparatus, cause health hazards and make environment unfriendly, so heterogeneous catalyst got priority for safe and efficient reaction [9]

Acidic ion exchange method followed ion exchange mechanism using organic catalyst like Amberlite IR-120. It is insoluble and yellow colored beads having porous surface. Peroxycarboxylic acid reacts with catalyst through its porous surface. It acts as acidic cation exchange catalyst (AIEC) having active replaceable hydrogen, bonded with sulphonic acid gives functionally active site of polystyrene which mainly initiates the transfer of hydrogen ion within the structure as counter ion movement.

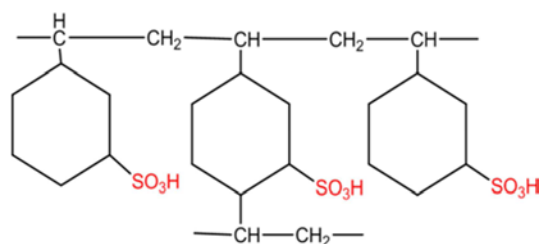


Figure 1. Structure of Amberlite IR-120.

Acidic ion exchange method has proved beneficial than traditional method owing to

Enhanced selectivity.

Using suitable inert solvent.

Counter ion exchanging mechanism.

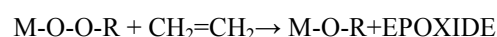
Controlled side product formation.

By maintaining appropriate temperature conditions [10]

In enzymatic catalysis based technique, enzymes are being used as a catalyst. Esterase and immobilized lipase prominently used to provide high yield reaction and stable resin but unfavorable to cost effect [7]. Besides this reaction should be preceded with great care and on controlled temperature condition because enzymes will get denatured

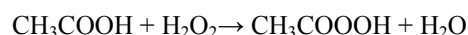
and lost its catalytic activity on elevated temperature conditions [10]

In halohydrin method of epoxidation, olefins are mixed with hypohalous acid in the presence of strong alkali for the epoxidation of ethlenic unsaturation but cannot be conducted because of harmful environmental effects. The epoxidation using transition metallic catalyst includes formation of peroxometallic specie by the combination of early transitional metals (like Mo, V, Ti & W) with alkyl peroxides results in (M-O-OR) which acts as oxygen transferring agent to a nucleophile (ethylenic unsaturation) to form epoxide ring. Metals never undergo oxidation change but help to increase electrophilic character by withdrawing electron density of -O-O- bonds [7].



Reaction mechanism is kinetically preceded in two phase steps. Reaction starts with the formation of initiator like peroxy-carboxylic acids by excitingly combination of hydrogen peroxide with carboxylic acids using a catalyst in aqueous phase. It is solid-liquid phase reaction. This leads to next step, i.e. combination of peroxy-carboxylic acid with unsaturated fatty acid in oil phase for completion of reaction [10].

FIRST STEP



SECOND STEP



The formation of peroxy-carboxylic acid has significance because it transfer active oxygen atom to the C=C centre of fatty acid to form epoxide. Two types of carboxylic acids can be used for the synthesis of peroxy-carboxylic acid, i.e. formic acid and acetic acid. former has relatively 10% less rates of conversion of ethylenic unsaturation to epoxide based product. Therefore, acetic acid is preferably used due to tremendous features like its availability, high epoxidation efficiency, less unwanted by-products formation, save economy and low kinetics rates to avoid rapidly degradation of hydrogen peroxide to save its active oxygen atom [9]. Therefore, a catalyst is used to compensate the rate of reaction. Choice of catalyst is a burning issue for researchers because whole method depends upon nature and status of catalyst. It may have followed by homogeneous or heterogeneous catalysis in which homogeneous catalysis cause hindrance in separation of products and recovery of catalyst than heterogeneous catalysis.

Variation in the mixture of different products formation depends upon various factors such as probability of epoxidation of unsaturation points of fatty acids. Secondly, physical parameters may affect the efficiency of reaction like, temperature condition, reactants purity, catalyst concentration, stirring speed and nature of catalyst, hydrogen peroxide to acetic acid ratio, hydrogen peroxide to vegetable

oil ratio and carboxylic acid to fatty acid ratio [10]. Stoichiometrically, it is calculated that one mole of carboxylic acid is required for each mole of unsaturation of linoleic acid and oleic acid. But less concentration of carboxylic acid is recommended to get maximum product and to avoid side product formation. Similarly hydrogen peroxide should adjust upto one mole of each double bond present in one mole of oil. One mole of hydrogen peroxide is needed for epoxidation of oleic acid and two moles required for linoleic acid because linoleic acid has two double bonds in it [11].

Temperature is supposed to be a critical stage for the production and stability of product. Optimum temperature condition is adjusted in the range of 55-65°C, this give stable epoxide ring which may degrade with the increase of temperature [12]. In spite of temperature, a suitable inert solvent also effect ring stability which needed to avoid ring opening during the reaction mixture. Best recommended solvents being used are toluene and benzene because they restrict ring opening and maintain its stability. Stirring speed may have great impact on the rate of reaction. Its range may adjust within the range of 500-2000 rpm to get maximum yield while adjusting other factors. The main objective of this research functionally based upon preferably application in different fields with conditionally variation in modification of oil.

2. Materials & Methods

Watermelon seed oil was obtained from central chemicals (Abkari road Lahore, Pakistan) and glacial acetic acid (99.7% wt.) of A.R grade was obtained by B.D.H. specialties pvt. Limited. The H_2O_2 (30% wt.) of A.R grade and Amberlite I.R-

120 with sulfonated polystyrene type cation exchange resin in H^+ form was used as catalyst & obtained from Alpha Aldrich specialties pvt. Limited. Toluene, diethyl ether, Anhydrous Na_2SO_4 were purchased from B.D.H specialties pvt. Limited. For analytical purpose, NaOH, Na_2CO_3 , thiosulphate crystal violets were obtained from BDH Company of A.R. grade.

2.1. Procedure

The epoxidation of watermelon seed oil was carried out in 1000ml three neck flask adjusted with a thermometer, condenser and equipped with a electrical stirrer. The whole assembly was immersed in water bath. 200ml of watermelon seed oil with equal mass of toluene was taken in a reactor/1 lit. Three neck flask with an appropriate amount of glacial acetic acid and Amberlite I.R-120 H^+ were loaded in the reactor and mixture was stirred for about 30 minutes. Then the required amount of 30% aq. H_2O_2 solution was gradually added drop wise into the reaction mixture at a constant rate and addition was completed in 1hr.

The reaction was continued further at desired time for desired product. Samples were drawn out intermittently, after completion of addition of H_2O_2 solution drop wise at zero time. The reaction mixture was cooled at room temperature. The samples were extracted with diethyl ether and washed with spray of water and layers were separated. The organic layer again washed with water and dried with anhydrous magnesium sulphate. The collection of acid free samples were removed the trace amount of solvents by heating the samples to 50°C under a vacuum for four hours and then desired product was analyzed for iodine value & equivalent epoxy content.

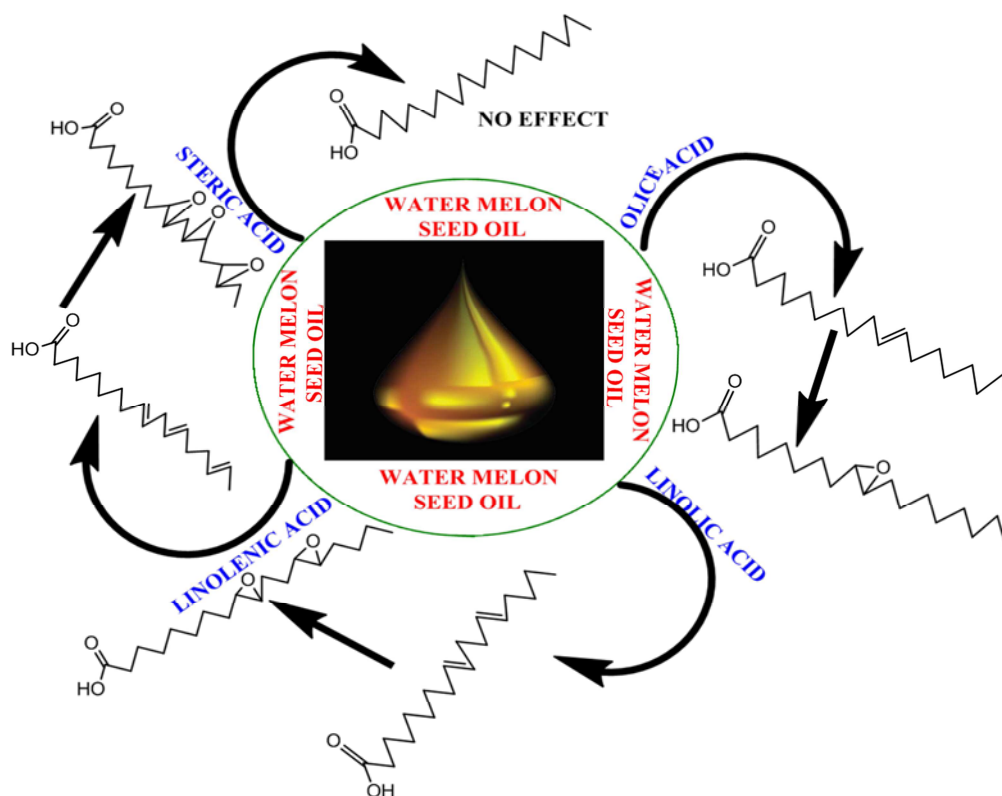


Figure 2. Epoxidation of *Citrullus Lanatus* (watermelon) seed oil.

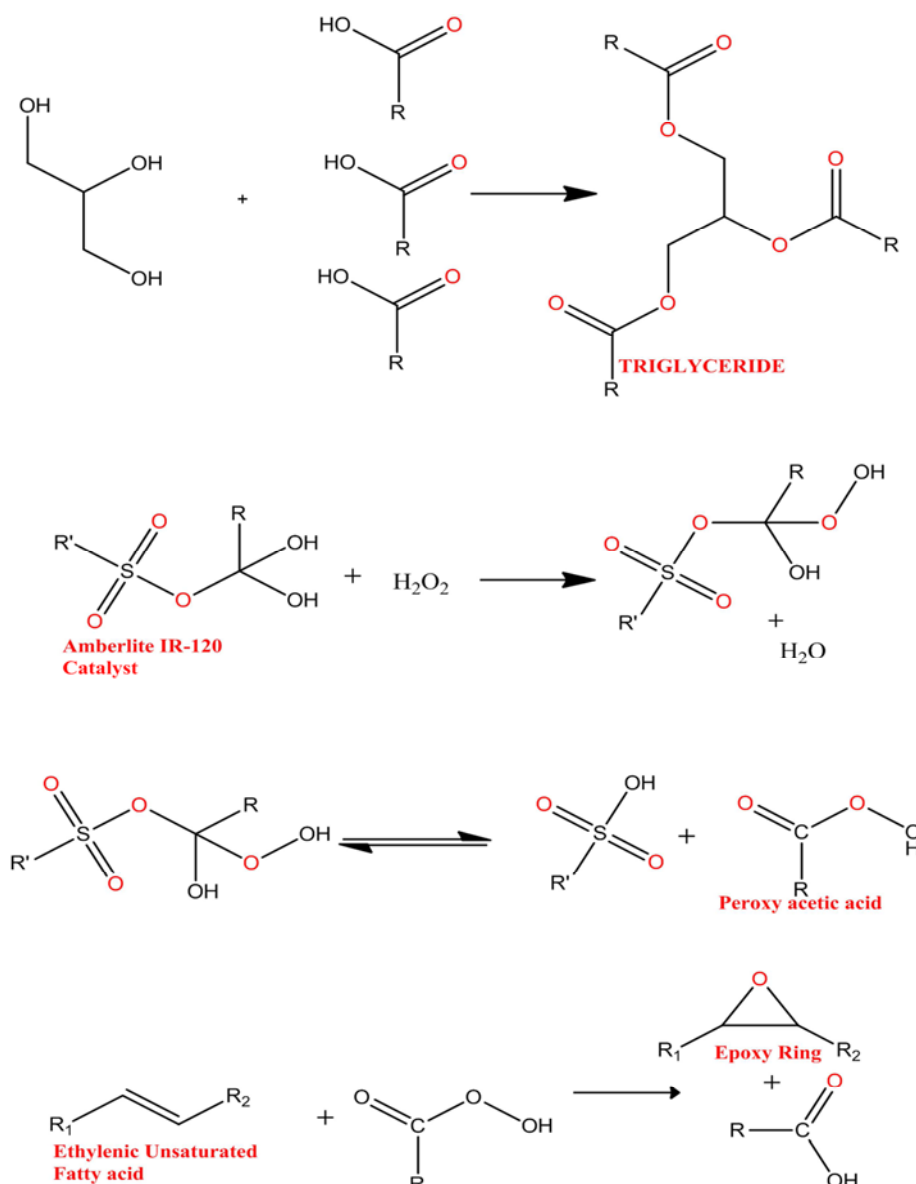


Figure 3. Chemistry of epoxidation of WMSO.

2.2. Analytical Technique

The percentage of epoxy oxygen content of sample is determined by a standard titration method [5]. Iodine value of collected sample was determined by wij's method (paquot, 1979) (ketaren. 2005) (Siggia. 1963) [14]. The mathematical calculation of reactants, required for the epoxidation of water melon seed oils. Some typical fatty acid composition with its mole wt. profile by for x WMSO oil is presented in table 1.

Table 1. Fatty acid composition and their molecular weights present in 'X'WMSO oil.

Fatty acids (C atoms: double bonds)	Mol. Formula	Composition (wt%)	Mol. weight
linolenic acid (18:3)	$\text{C}_{18}\text{H}_{30}\text{O}_2$	1.02	278.43
Linoleic acid (18:2)	$\text{C}_{18}\text{H}_{32}\text{O}_2$	62.2	280.45
Oleic acid (18:1)	$\text{C}_{18}\text{H}_{34}\text{O}_2$	14.2	282.46
Stearic acid (18:0)	$\text{C}_{18}\text{H}_{38}\text{O}_2$	10.2	284.45
Palmitic acid (16:0)	$\text{C}_{16}\text{H}_{30}\text{O}_2$	12.2	254.46

2.2.1. Watermelon Seed Oil Calculations

Total mole (n_i) of 'X' WMSO oil is expressed as concentration of double bond in oil.

Volume (v) of WM seed oil = 200 ml

Density (d) of WM seed oil = 0.914g/m

Mass (M) of WM seed oil = $d \times v = 0.914 \times 200 = 182.8 \text{ g}$

$$n = \frac{\text{T.mass} \times \text{wt}\%}{\text{actual given weight}} \quad (1)$$

The value of n for different fatty acids composition can be calculated by using eq. 1

$$n \text{ for linolenic acid} = \frac{0.102 \times 182.2}{278.43} = 0.006696$$

$$n \text{ for linoleic acid} = \frac{0.622 \times 182.2}{280.45} = 0.405425$$

$$n \text{ for oleic acid} = \frac{0.142 \times 182.2}{282.45} = 0.091898$$

$$n_t = 0.006696 + 0.405425 + 0.091898 = 0.504 \text{ mol}$$

Total moles of WMSO oil = 0.504 mole

Acetic acid

Mole ratio of A.A. to Double bond = 0.5%

mol. Wt. of Glacial acetic acid = 60.05 g/mol

Density = 1.05 g/cm³

Mole of acetic acid (0.5%) $n_t = 0.50 \times 0.504 = 0.252$ mole

Mass of acetic acid = mole \times mol.wt. = $0.252 \times 60.05 =$

15.13 g

Mass of glacial acetic acid = $100/99.5 \times 15.13 = 15.20$ g

Vol. of glacial A.A = $15.20 / 1.05 = 14.47$ ml

Hydrogen peroxide H₂O₂

Mole of H₂O₂ to Double bond ratio = 1.5:1

H₂O₂ mol. Wt. = 34.01

Density = 1.10 g/ml

Mole of H₂O₂ = $1.5 \times 0.504 = 0.756$ mol

Mass of H₂O₂ = $0.756 \times 34.01 = 25.71$ g

Mass of H₂O₂ solution = $100/30 \times 25.71 = 85.7$ g

Vol. of H₂O₂ needed = $85.7 / 1.10 = 77.90$ ml

Amberlite Catalyst

Mass of amberlite in the mixture is 3% of total mass of

H₂O₂ & acetic acid.

Amberlite (99 wt%) average mol. Wt. = 96.6

Density = 1.02 g/ml

Mass = $(3/100) \times (H_2O_2 + CH_3COOH) = (3/100) \times (25.71$

$+ 15.20) = (3/100) \times 40.91 = 1.22$ g

Vol. of amberlite = $1.22 / 1.02 = 1.19$ ml

2.2.2. Determination of Iodine Value & Conversion

In order to determine conversion of iodine value, the iodine value of 'X' WMs oil can be calculated by using this following equation.

$$\text{Iodine value (I.V.)} = \frac{(B-S) \times M \times 12.69}{w} \quad (2)$$

Where as

S = vol. of Na₂S₂O₃ solution required for titration of sample (ml)

B = vol. of Na₂S₂O₃ solution required for titration of blank (ml)

W = weight of sample used (g)

M = molarity of Na₂S₂O₃ (0.1 M)

Initial value of "X" WMs oil expressed as iodine value at time t = 0h

Molarity (M) = 0.10 M

Weight (W) = 0.17 g

B₁ = 20.65 ml S₁ = 5.30 ml

B₂ = 20.50 ml S₂ = 5.35 ml

B₃ = 20.65 ml S₃ = 5.25 ml

B_{av} = 20.60 ml S_{av} = 5.30 ml

I.V. = $\frac{(20.60 - 5.30) \times 0.1 \times 12.69}{0.17} = 114.7$ g iodine / 100g oil

Conversion of iodine value (%X):

$$\%X = \frac{I.V_0 - I.V}{I.V_0} \times 100\% \quad (3)$$

Where

I.V₀ = initial iodine value

I.V. = iodine value at certain condition

Calculation at temperature 60°C

Reaction Time 't' = 1 hr

W = 0.17 g S₁ = 8.8 ml

S₂ = 8.5 ml S₃ = 8.6 ml

S_{av} = 8.6 ml

I.V. = $\frac{(20.60 - 8.6) \times 0.1 \times 12.69}{0.17} = 89.57$ g iodine / 100g

$\%X = \frac{114.7 - 89.57}{114.7} \times 100\% = 21.90\%$

Reaction Time 't' = 2 hr

W = 0.17 g S₁ = 9.8 ml

S₂ = 9.8 ml S₃ = 9.8 ml

S_{av} = 9.8 ml

I.V. = $\frac{(20.60 - 9.8) \times 0.1 \times 12.69}{0.17} = 80.61$ g iodine / 100g oil

$\%X = \frac{114.7 - 80.61}{114.7} \times 100\% = 29.72\%$

Reaction Time 't' = 3 hr

W = 0.17 g S₁ = 9.90 ml

S₂ = 9.91 ml S₃ = 9.90 ml

S_{av} = 9.90 ml

I.V. = $\frac{(20.60 - 9.90) \times 0.1 \times 12.69}{0.17} = 79.87$ g iodine / 100g oil

$\%X = \frac{114.7 - 79.87}{114.7} \times 100\% = 30.30\%$

Reaction Time 't' = 4 hr

W = 0.17 g S₁ = 10.5 ml

S₂ = 10.6 ml S₃ = 10.6 ml

S_{av} = 10.6 ml

I.V. = $\frac{(20.60 - 10.6) \times 0.1 \times 12.69}{0.17} = 74.64$ g iodine / 100g oil

$\%X = \frac{114.7 - 74.64}{114.7} \times 100\% = 34.92\%$

Reaction time 't' = 5 hr

W = 0.17 g S₁ = 11.8 ml

S₂ = 11.8 ml S₃ = 11.7 ml

S_{av} = 11.8 ml

I.V. = $\frac{(20.60 - 11.8) \times 0.1 \times 12.69}{0.17} = 65.68$ g iodine / 100g oil

$\%X = \frac{114.7 - 65.68}{114.7} \times 100\% = 42.73\%$

Reaction time 't' = 6 hr

W = 0.17 g S₁ = 12.6 ml

S₂ = 12.6 ml S₃ = 12.7 ml

S_{av} = 12.6 ml

I.V. = $\frac{(20.60 - 12.6) \times 0.1 \times 12.69}{0.17} = 59.71$ g iodine / 100g oil

$\%X = \frac{114.7 - 59.71}{114.7} \times 100\% = 47.94\%$

2.2.3. Determination of Oxiran Oxygen Content

The number of oxiran groups indicated by the percentage of oxiran oxygen content is calculated by using following formula.

$$\text{Oxygen Content} = \frac{(B-S) \times M \times 16 \times 100}{W \times 1000} \quad (4)$$

Where

S = vol. of NaOH solution required for titration of sample

(ml)

B = vol. of NaOH solution required for titration of blank

(ml)

W = weight of sample used (g)

M = molarity of NaOH (0.1 M)

B₁ = 16.7 ml B₂ = 17.2 mlB₃ = 16.7 ml B_{av} = 16.7 ml

Temperature = 60°C

Reaction time 't' = 1 hr

W = 0.17 g S₁ = 15.7 mlS₂ = 15.8 ml S₃ = 15.8 mlS_{av} = 15.7 ml

$$\% \text{ oxirane} = \frac{(B-S) \times M \times 16 \times 100}{W \times 1000}$$

$$\% \text{ oxirane} = \frac{(16.7-15.7) \times 0.1 \times 16 \times 100}{0.17 \times 1000} = 0.94\%$$

Reaction time 't' = 2 hr

W = 0.17 g S₁ = 15.1 mlS₂ = 15.2 ml S₃ = 15.0 mlS_{av} = 15.1 ml

$$\% \text{ oxirane} = \frac{(16.7-15.1) \times 0.1 \times 16 \times 100}{0.17 \times 1000} = 1.50\%$$

Reaction time 't' = 3 hr

W = 0.17 g S₁ = 14.7 mlS₂ = 14.8 ml S₃ = 14.6 mlS_{av} = 14.7 ml

$$\% \text{ oxirane} = \frac{(16.7-14.7) \times 0.1 \times 16 \times 100}{0.17 \times 1000} = 1.88\%$$

Reaction time 't' = 4 hr

W = 0.17 g S₁ = 14.2 mlS₂ = 14.3 ml S₃ = 14.4 mlS_{av} = 14.3 ml

$$\% \text{ oxirane} = \frac{(16.7-14.3) \times 0.1 \times 16 \times 100}{0.17 \times 1000} = 2.25\%$$

Reaction time 't' = 5 hr

W = 0.17 g S₁ = 13.8 mlS₂ = 13.9 ml S₃ = 14.0 mlS_{av} = 13.9 ml

$$\% \text{ oxirane} = \frac{(16.7-13.9) \times 0.1 \times 16 \times 100}{0.17 \times 1000} = 2.63\%$$

Reaction time 't' = 6 hr

W = 0.17 g S₁ = 13.5 mlS₂ = 13.6 ml S₃ = 13.7 mlS_{av} = 13.6 ml

$$\% \text{ oxirane} = \frac{(16.7-13.6) \times 0.1 \times 16 \times 100}{0.17 \times 1000} = 2.91\%$$

3. Results and Discussion

Experimentally determined characteristics values of WMSO oil can be summarized as molecular mass (M) is 182.8g, iodine value (IV) is 115, specific gravity at room temperature is 0.914, Acid value (AV) measured as mass of KOH (g)/100 g is 1.00, saponification value (SV) calculated as mass of KOH (mg)/100g is 188, linoleic acid carbon ratio 18:2, oleic acid carbon ratio is 18:1 [16]. Linoleic acid contributes majorly in relative conversion to epoxidation owing to greater unsaturation level than linolenic acid. All components of fatty acid oil are enlisted table 1 along their physical properties. Epoxidation of WMSO oil can be studied by some parameters which may cause difference in production rate of desired product. Each factor has tremendously relationship with epoxidation rate.

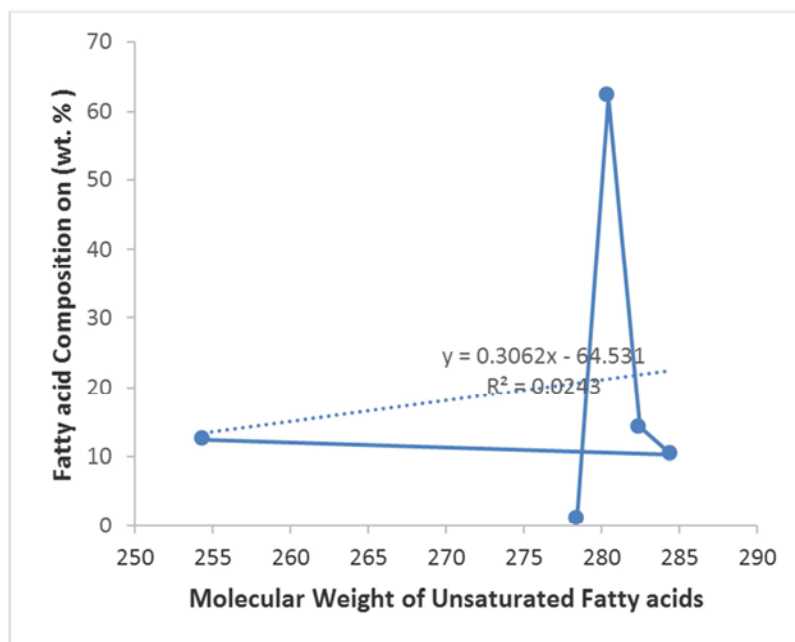


Figure 4. Fatty acid composition and their molecular weights present in 'X'WMSO oil.

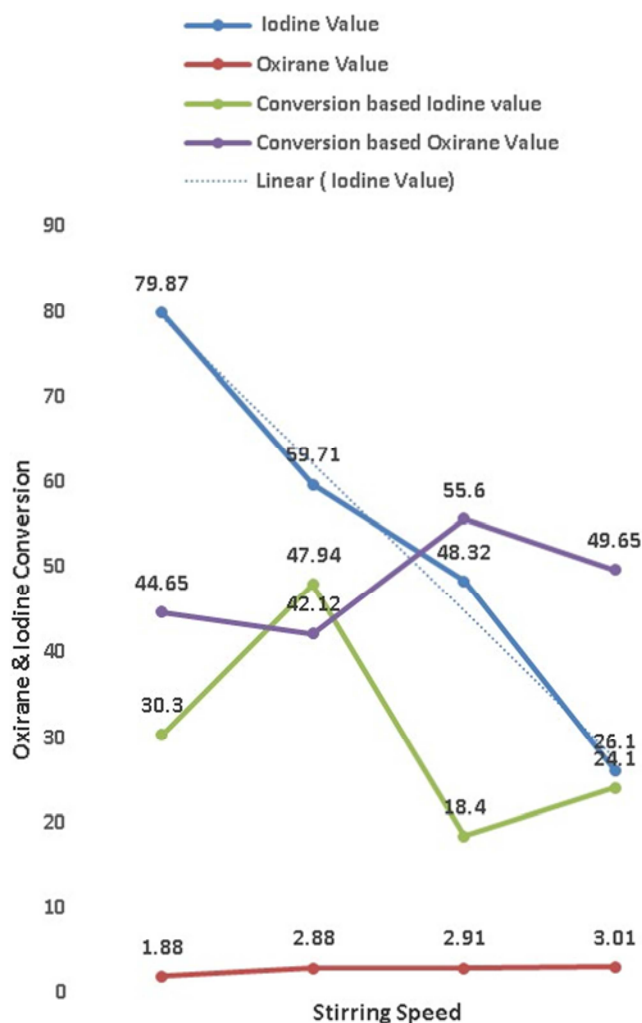
Effect of Stirring Speed:

For the estimation of effect of mechanical stirring speed, the chemical reaction is conducted at different stirring speed having 500 to 2500 rpm ranging but reaction should be kinetically controlled at such high speed. A noticeable change in production of oxirane was observed with variation of stirring speed but this production is consistently increasing up to 1000 rpm speed with time duration of 6 hrs supposing mass transfer resistance up to zero under specific condition of temp and other variables.

Table 2. Oxirane Conversion at different stirring speed.

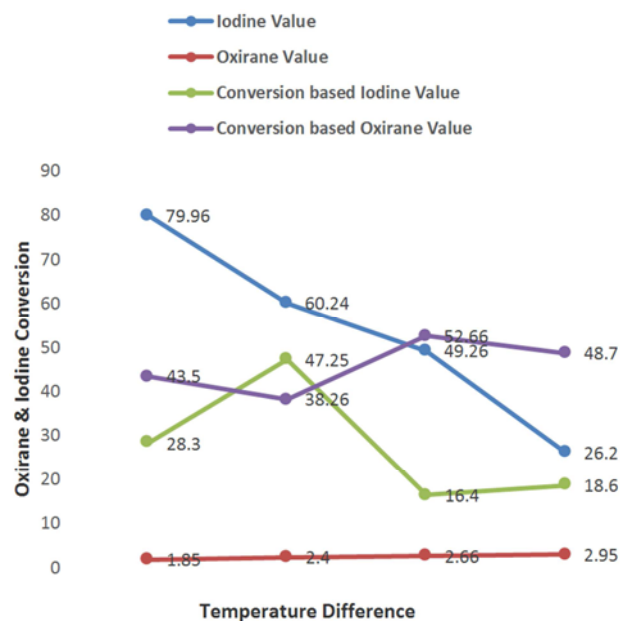
Lipinski properties	Stirring speed (rpm)			
	500rpm		100rpm	
Time (hrs)	3	6	3	6
Iodine value (gI ₂ /100g oil)	79.87	59.71	48.32	26.10
Conversion (Based On iodine value)	30.30	47.94	18.40	24.10
Oxirane value	1.88	2.88	2.91	3.01
%Epoxidized double Bond (based on Oxirane value)	44.65	42.12	55.60	49.65

Conditions: H₂O₂ per mole of double bond=1.5, CH₃COOH per mole of Double bond=0.5 Amberlite IR-120 loading=3%, Temperature=60°C

**Figure 5.** Oxirane and iodine Conversion at different stirring speed.

Effect of Temperature:

Temperature is the most kinetically significant factor which affects reaction directly but in addition to temperature, time of proceeding reaction correlates simultaneously for maximum oxirane ring production. High temperature results in favor of maximum, it should be very careful to conduct reaction at high temperature because opening of oxirane ring is being started at high temperature but stability of oxirane ring is observed at lower temperature. Reaction was proceeded at different ranges of temperature along with time variation but 40-60°C with 6 hours timing give favorable results which is illustrated by graph and table.

**Figure 6.** Effect of temperature on oxirane and iodine value.**Table 3.** Oxirane Conversion at different temp.

Lipinski properties	Temperature °C			
	40°C		60°C	
Time (hrs)	3	6	3	6
Iodine Value (g I ₂ /100g Oil)	79.96	60.24	49.26	26.20
Conversion (Based on Iodine Value)	28.30	47.25	16.40	18.60
Oxirane Value	1.85	2.40	2.66	2.95
% Epoxidized double bond (Based on Oxirane Value)	43.50	38.26	52.66	48.70

Conditions: H₂O₂ per mole of double bond=1.5, CH₃COOH per mole of Double bond=0.5, Amberlite IR-120 loading=3%, Temperature=60°C RPM=500

Effect of Hydrogen Peroxide to Fatty Acid Unsaturation Ratio:

Likewise stirring speed, it is very focusing point to maintain hydrogen peroxide concentration to fatty acid unsaturation molar ratio to attain maximum yield. It is observed that production rate increases with the increase of this ratio. Reactions were conducted at 1.1 and 1.5 values by varying concentration of hydrogen peroxide and keeping

fatty acid unsaturation constant. It is very clear from results and graph that shows maximum relative oxirane production on 1.5:1 of hydrogen peroxide to fatty acid unsaturation ratio. Beyond this value, no doubt, production rate also enhances with the increase in H_2O_2 concentration but one problem is being faced that oxirane ring stability decreases above 1.5 value. To overcome this hurdle, 1.5:1 ratio is adjusted as optimum condition.

Table 4. Oxirane Conversion & Iodine Value at Molar ratio of H_2O_2 to Double bond.

Lipinski properties	Molar ratio of H_2O_2 to Double bond			
	1.1		1.5	
Time (hrs)	3	6	3	6
Iodine Value (g I_2 /100g Oil)	79.22	46.96	42.31	26.18
Conversion (Based on Iodine Value)	36.14	48.32	24.16	22.25
Oxirane Value	1.80	2.18	2.68	2.70
% Epoxidized double bond (Based on Oxirane Value)	40.26	38.84	50.42	49.36

Conditions: H_2O_2 per mole of double bond=1.5, Amberlite IR-120 loading=3%, Temperature=60°C, RPM=500

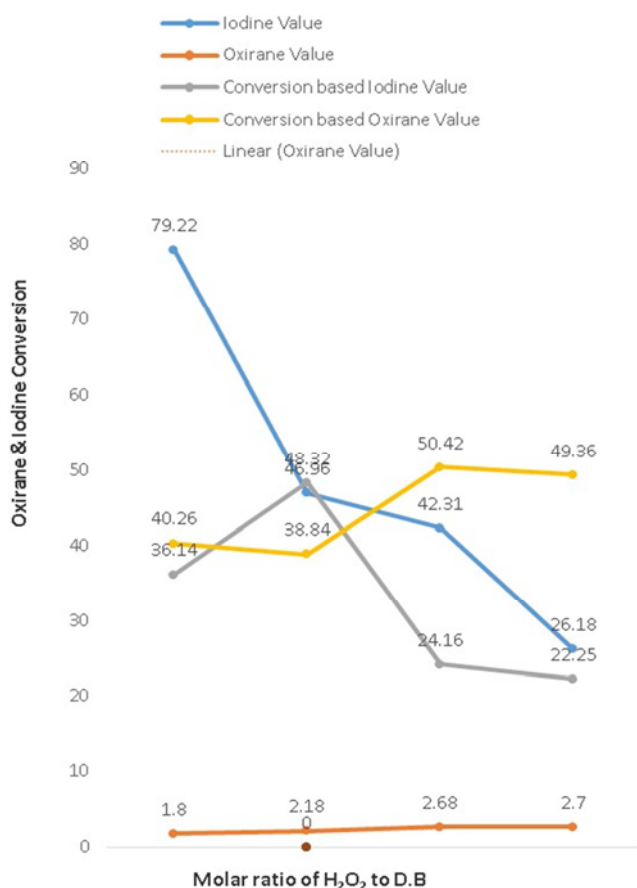


Figure 7. Relation of Molar ratio of H_2O_2 to Double bond with Oxirane Conversion & Iodine Value.

Effect of Acetic Acid to DoubleBond:

Glacial acetic acid act as very important initiator for the synthesis of peroxy acetic acid to proceeded reaction further. So its quantity with respect to fatty acid unsaturation also has

significance for oxirane production. It also acts as medium solvent for the production of oxirane. Experiments were conducted on two different values of acetic acid to fatty acid unsaturation ratio but results explore that 0.5:1 ratio yields more oxirane content while iodine value at least.

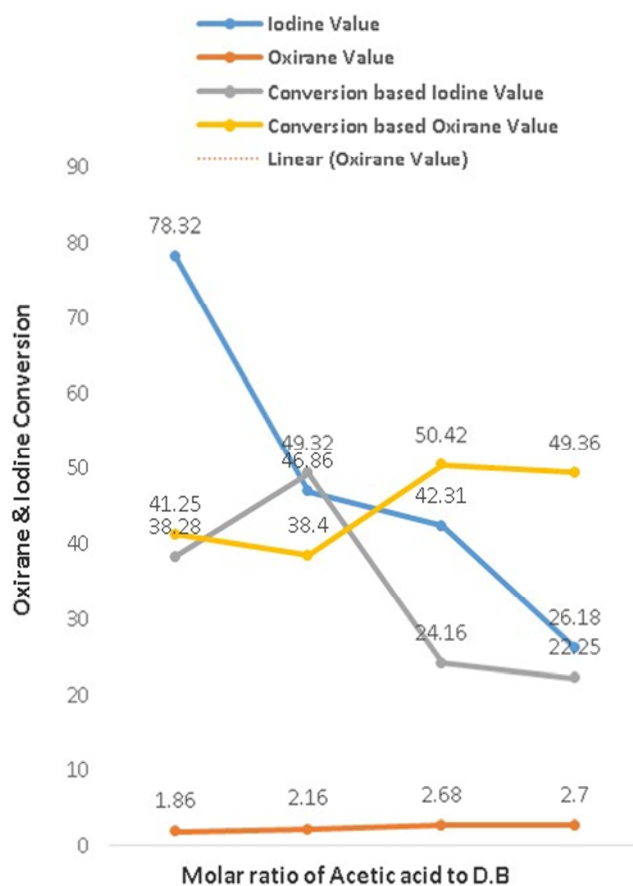


Figure 8. Effect of molar ratio of acetic acid to double bond on oxirane and iodine value.

Table 5. Oxirane Conversion & Iodine Value at Molar ratio of Acetic Acid to Double bond.

Lipinski properties	Molar ratio of Acetic acid to Double bond			
	0.25		0.5	
	3	6	3	6
Iodine Value (g I ₂ /100g Oil)	78.32	46.86	42.31	26.18
Conversion (Based on Iodine Value)	38.28	49.32	24.16	22.25
Oxirane Value	1.86	2.16	2.68	2.70
% Epoxidized double bond (Based on Oxirane Value)	41.25	38.40	50.42	49.36

Conditions: CH₃COOH per mole of double bond=0.5, Amberlite IR-120 loading=3%, Temperature=60°C, RPM=500

Effect of Nature of Catalyst:

It mostly counts that nature of catalyst should suitable with the phase of other reaction mixture to obtain high production rate. In this experiment, Amberlite, the heterogeneous non-aqueous catalyst is used while keeping drawbacks in consideration of other mineral acids as catalyst that causes opening of oxirane ring [9].

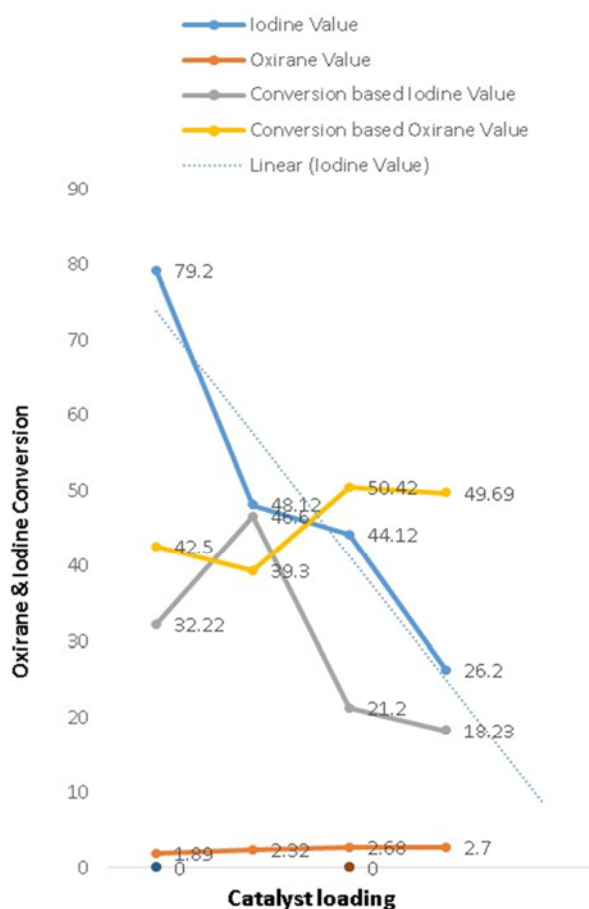
Effect of Concentration of Catalyst:

Concentration of catalyst relates directly with oxirane production rate along with concentration of H₂O₂ and acetic acid. Catalyst concentration is taken as total mass of concentration of H₂O₂ and acetic acid. Experiments were conducted with different loadings of catalyst at 2.5% and 3%. But 3% catalyst concentration show significant oxirane ring production with maximum yield than others has less production rate.

Table 6. Oxirane Conversion & Iodine Value at Catalyst loading.

Lipinski properties	Amberlite IR-120 Loading%			
	2.5%		3%	
Time (hrs)	3	6	3	6
Iodine Value (g I ₂ /100g Oil)	79.20	48.12	44.12	26.20
Conversion (Based on Iodine Value)	32.22	46.60	21.20	18.23
Oxirane Value	1.89	2.32	2.68	2.70
% Epoxidized 42.50 double bond (Based on Oxirane Value)		39.30	50.42	49.69

Conditions: H₂O₂ per mole of double bond=1.5, Acetic Acid per mole of Double bond=0.5, Temperature=60°C, RPM=500

**Figure 9.** Effect of catalyst loading on oxirane and iodine value.

4. Conclusion

In-situ epoxidation process WMSO oil could be epoxidized with successfully rate by reacting glacial acetic acid with hydrogen peroxide (By employing proxy acetic acid generated in-situ) at optimum temperature condition. By this process, the epoxidation of WMSO oil consider to be a more convenient and economically valuable method, which utilized especially in plasticizer and stabilizer used in polymer.

The epoxidation of WMSO oil enhance the rate of as valuable method that which show the properties of plasticizer and stabilizer used in polymer. The epoxidation of WMSO oil can be confirmed by oxirane content value, FTIR, ¹H-NMR, ¹³C-NMR and LC-MS analysis.

The present study on the epoxidation of WMSO oil has the following certain optimum conditions which include temperature of at 60°C, Rpm speed 500, Timing 6 hrs, hydrogen peroxide to FU ratio of 1.5:1, Acetic acid to FU ratio of 0.5:1 and the Amberlite I.R-120 cation exchange resin loading was 3% by weight of the total weight of hydrogen peroxide and acetic acid.

References

- [1] Koocheki, S. M. A. Razavi, E. Milani, T. M. Moghadam, M. Abedini, S. Alamatyian, and S. Izadkhah, Department of Food Science and Technology, Ferdowsi University of Mashhad (FUM), P. O. Box. 91775-1163, Mashhad, Iran, 2007.

- [2] BaharakSajjadi Abdul Aziz, Abdul Raman, Hamid reza Arandiyani, Renewable and Sustainable Energy Reviews, Volume 63, September 2016, Pages 62-92, october-2016.
- [3] Duduyemi, Oladejo, Adebajo S. A, Oluoti Kehinde, August 2013, International Journal of Science & Technology research vol. 2, issue 8.
- [4] Petrovic Z. S., Zlatanovic A., Lava C. C. Epoxidation of soya bean oil in toluene with peroxyacetic acid and peroxyformic acids-kinetics and side reactions. European Journal of Lipid Science and Technology 104 (5): 293-299.5. Okieimen F. E., Bakare O. J. & Okieimen C. O. (2002).
- [5] Zengshe Liu, Jie Chen, Gerhard Knothe, Xiaonan Nie, and Jianchun Jiang, *ACS Sustainable Chem. Eng.*, 2016, 4 (3), pp 901–906.
- [6] J. Braz. Chem. Soc. vol. 22 no. 12 São Paulo Dec. 2011.
- [7] Luis Alberto Rios aus Medellín, Colombia, Tag der mündlichen Prüfung: 11. April 2003, M.Sc-Chemisch Ingenieur.
- [8] Padmasiri K. Gamage, Micheal O'Brien and Laleen Karunanayake Epoxidation of some vegetable oils and their hydrolysed products London Metropolitan University, Holloway Road, London N7 8DB, UK. Department of Chemistry, Faculty of Applied Science, University of Sri Jayewardenepura, Gangodawila, Nugego.
- [9] Cooney, T. I., Cardona, F., & Tran-Cong, T. (eddBE2011 Proceedings 106 Energy, Environment and Sustainability).
- [10] Tayde Saurabh., Patnaik M. Bhagt S. L., Renge V. C. epoxidation of vegetable oil review. IJAET/VOL.II/ISSUE IV/October –December 2011//491-501.
- [11] Wei Liu, Jingnan Chen, Ruili Liu, Yanlan Bi, Journal of the American Oil Chemists' Society, November 2016, Volume 93, Issue 11, pp 1479–1486.
- [12] Sinadinovic-Fiser, S., Jankovic, M., & Petrovic, Z. S. (2001). Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. Journal of the American Oil Chemists Society, 78 (7), 725-731.
- [13] Goud, V. V., Pradhan, N. C., & Patwardhan, A. V. (2006). Epoxidation of karanja (*Pongamia glabra*) oil by Hydrogenperoxide. Journal of the American Oil Chemists Society, 83 (7), 635-640.
- [14] Ketaren S (2005). Edible oils and fats, UI-Press, Jakarta. P. 145.
- [15] Jun L. Zheng, Johan Wärmå, Tapio Salmi, Fabrice Burel, Bechara Taouk, Sébastien Leveneur, 5 Oct 2015.
- [16] Angelini et al., 1997; Ncube et al., 1998; Warwel et al., 2004.