Epoxidation of Jatropha Oil

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Abstract: Compared to saturated components, monounsaturated fatty acids is better for biofuel. The biofuel's unsaturation offers oxidative stability and low-temperature fluidity. Vegetable oils that are high in oleic, linoleic, and linolenic acyl gatherings may become unsaturated, which may result in the introduction of useful social phenomena like epoxides. Epoxidized unsaturated fat auxiliaries from vegetable sources are particularly useful in a variety of applications, including as stabilizers and plasticizers in polymers, additives in oils, components in plastics, and intermediates for a huge variety of products. Jatropha oil contains a mixture of unsaturated fatty acids, such as oleic and linoleic acids. However, the high unsaturation decreases the oxidative stability of the oil thus the conversion of the unsaturation present in the jatropha oil into the oxirane ring increases the lubricative property of the oil. Thus, in this study, how different reaction parameters such as the stirring speed, the mole concentration of the hydrogen peroxide, the oxidizing agents like acetic acid, formic acid, and finally the reaction temperature affect the in situ epoxidation rate and the iodine value of the jatropha oil have been described.

Keywords: Jatropha oil, epoxidation rate, unsaturation, oxirane ring, iodine value

I. INTRODUCTION

The utilization of modified plant oils in the substance business is ending up being progressively entrancing and charming as a consequence of their openness from manageable resources. The unsaturation of vegetable oils high in oleic, linoleic, and linolenic acid get-togethers could introduce sensible reactions like epoxides. In particular, epoxidized unsaturated fat auxiliaries from vegetable sources can be used in various spaces, similar to stabilizers and plasticizers in polymers, as added substances in oils, as parts in plastics, and in urethane froths, and, when in doubt, as intermediates for a tremendous number of items. Various benefits of vegetable oils incorporate their superb lubricity, non-poisonousness, and biodegradability; In every industry, they could be used in place of mineral oil-based greases and engineered esters. Compared to mineral-based lubricants, vegetable oils are significantly more biodegradable. Vegetable oils, on the other hand, are incompatible with direct lubrication applications due to their propensity to hydrolyze, oxidize, and thermally decompose.

Figure 1: Lubrication of vegetable oil

(Source: https://pubs.acs.org/cms/10.1021/acs.iecr.1c03974/asset/images/acs.iecr.1c03974.social.jpeg_v03)

The oxygen rapidly alters the twofold bonds in the unsaturated fat chains. High twofold bonds are found in a couple of vegetable oils like sunflower, soybean, jatropha, rapeseed, nut, cotton, and palm, etc. are the primary focus of bio-lubricant production. In tropical climates, palm, peanut, soybean, and jatropha oils are readily available.

The Bronsted acid can be homogeneous, such as phosphoric acid, and sulfuric, and additionally heterogeneous, for example, zeolites and ion exchange resins. This epoxidation reaction is a complex method that follows many reaction steps from which some of the reaction steps occurred in the aqueous phase, some can occur in the organic reaction page, and the rest of the reaction phase can occur in the water-oil interphase. However, the reaction mechanism for the in situ epoxidation by using the homogeneous catalyst can be described through different reaction steps, such as -

(i) Peroxyacetic acid formation in the presence of a catalyst in the aqueous phase

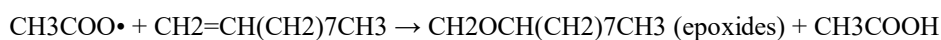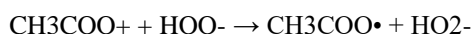$$CH_3COOH + H_2O_2 \leftrightarrow CH_3COOOH + H_2O$$

The reaction for the peroxyacetic acid formation is taken out in the presence of an acid catalyst and in the aqueous medium. This reaction is very fast and quickly reaches the equilibrium stage. The synthesized peracetic acid is quietly soluble in the oil medium. Here, the moderately soluble peracetic acid helps to prevent the movement of hydrogen peroxides into the organic phase and the starting of an epoxidation reaction of the double bonds present in the vegetable oil.

(ii) Peroxyacetic acid transfer from the aqueous phase to the oil phase

$$CH_3COOOH \rightarrow CH_3COO^+ + HOO^-$$

Here, the prevention of the epoxidation reaction of the double bonds present in the vegetable oil and the movement of the hydrogen peroxides into the organic phase is important, thus, the peroxyacetic acid must be moved from the aqueous phase to the oil phase.

(iii) Decomposition of peroxyacetic acid to form epoxide or oxirane and the release of acetic acid

$$CH_3COO^+ + HOO^- \rightarrow CH_3COO^\bullet + HO_2^-$$

$$CH_3COO^\bullet + CH_2=CH(CH_2)_7CH_3 \rightarrow CH_2OCH(CH_2)_7CH_3 \text{ (epoxides)} + CH_3COOH$$

The decomposition of the peroxyacetic acid is not so much desirable because it absorbs both the hydrogen peroxides and the peroxyacetic acid. Thus the decomposition of the peroxyacetic acid negatively impacts the whole epoxidation reaction. Therefore, to manage this loss, both the reactants such as the peracetic acid and the hydrogen peroxides must be added in excess in the reaction medium.

This reaction can occur in two steps where the first step is the formation of the acetic acid radical and the second step is the formation of the epoxides or the oxirane. And the reaction occurs between the peracetic acid and the unsaturations present in the vegetable oil. Here peracetic acid is the reactant, thus the produced epoxide is the epoxide of peracetic acid. The epoxidation reaction occurs

in the oil phase where the peracetic acid belongs from the aqueous medium and migrated into the oil medium and the unsaturation belongs from the oil medium.

(iv) Ring-opening or the degradation of the epoxide or oxirane in the oil phase

$CH_2OCH (CH_2)_7CH_3 + H_2O \rightarrow HOCH(CH_2)_7CH_3 + CH_2OH$
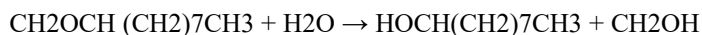
The ring of the epoxides opens in the oil phase. The ring of epoxide can be opened mainly in two ways either by the activity of the strong acid which is mainly present insolubly in the oil phase, and this reaction occurred in the interphase medium. And the type of ring opening occurs via the direct opening of the oxirane ring or the epoxide occurs by the nucleophilic attack. Here, the nucleophile is the acetic acid and this acetic acid can be found in the oil medium where it is partly dissolved.

(v) The transfer of acetic acid from the oil phase to the aqueous phase

$CH_3COOH + NaOH \rightarrow CH_3COO- + H_2O + Na+$
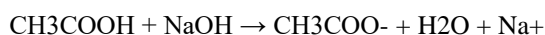
The final step of the epoxidation reaction is the transfer of the acetic acid from the oil medium to the aqueous medium.

Thus, the formation of the epoxide jatropha oil can be represented as follows -

$CH_2=CH(CH_2)_7CH_3 + H_2O_2 \rightarrow CH_2OCH(CH_2)_7CH_3 + CH_3COOH$

But, in the presence of acidic ion exchange resin as the heterogeneous catalyst, the reaction steps are broken down into many other subtypes. For example - the formation of the peroxy acid comprised many other subtypes such as the diffusion of the reactants through the catalyst pores, adsorption of the reactants on the surface of the catalysts, reaction on the surface of the catalyst, the diffusion of the product from the surface of the catalyst to the huge reaction medium. But, when the strong acidic catalyst have been used then there are no change can be observed in the reaction sequences with compare to the homogeneous reaction catalyst.

II. EXPERIMENTAL SECTION

2.1 Materials

Crude jatropha oil with the iodine number 105.68g/100g, formic acid, glacial acetic acid, 30% aqueous hydrogen peroxide, 95% sulphuric acid (H_2SO_4), iodine, anhydrous methanol (CH_3OH), sodium sulfate, sodium methoxide, anhydrous sodium sulfate (Na_2SO_4), Sodium hydrogen carbonate ($NaHCO_3$), crystal violet, and sodium hydroxide ($NaOH$).

2.2 Synthesis of Jatropha Oil

2.2.1 Epoxidation of Jatropha Oil

Epoxidized jatropha oil (EJO) can be produced in mass according to the strategies represented in the literature. Jatropha oil & formic acid can be heated to 40 °C in a water bath by constantly stirring. After the temperature reaches 40 °C, hydrogen peroxide is added dropwise to prevent overheating. The temperature is then raised and kept at 60 °C for five hours. Every 60 minutes, the oxirane oxygen content (OOC) is estimated. Following 5 hours of blending, the combination has carried down to normal temperature. After that, the aqueous layer is removed, and the epoxy is washed with too much-distilled water until it has a neutral pH. A rotary evaporator is used to get rid of any water that is still in the epoxy to get a pure EJO. $MgSO_4$ is used to dry the sample, and it is kept in a desiccator.

2.2.2. Oxirane Ring-Opening

Jatropha oil can likewise be switched over completely to other important synthetics through various substance responses, for example, oxirane ring opening. Oxirane rings are three-membered cyclic ethers that are available in numerous regular items and can be opened by different reagents.

A 1000 mL measuring beaker with a dropping pipe, thermometer, and magnetic stirrer is utilized for the responses. Ring-opening reagents like methanol, ethanol, and isopropanol are used to ring-open the epoxidized jatropha oil (EJO). A predetermined amount of ring-opening agent, water, and the sulfuric acid catalyst is added to the beaker. Until the various ring-opening agents reach their

boiling points, the mixture is continuously stirred. After that, EJO is added to the mixture, and the responses continue for 30 minutes before sodium bicarbonate is added to stop the response. After the deposit has been brought down to room temperature, it is thrown away. Vacuum refining eliminates the water and overabundance of ring-opening chemical agents.

III. RESULT AND DISCUSSION

In epoxidation runs, the following variables can be used: mixing speed somewhere in the range of 500 and 2500 fire up/min acidic destructive to-ethylenic unsaturation extent (mole per mole) 0.3-1.0 temperature 303-358 K, impulse stacking, hydrogen peroxide-to-ethylenic unsaturation extent (mole per mole) 0.8-2.5, formic destructive to-ethylenic unsaturation extent (mole per mole) 0.3-1.0, was conveyed as the weight level of regular stage, and is changed in the arrive at 5-20%. Following the epoxidation, relative fractional conversion to oxirane has plotted as a function of reaction time in each case.

3.1 Effect of stirring speed

To investigate the effect of stirring speed on catalytic epoxidation rate in triphase (solid catalyst, oil, and aqueous hydrogen peroxide) conditions, reactions have proceeded at a wide range of stirring speeds (500–2500 rev/min). With increasing stirring speed, it was observed that oxirane oxygen formation and ethylenic unsaturation conversion increased before leveling off around ca. 1500 rpm. The pace of response didn't altogether change over 1500 fire up/min. By the by, to guarantee that there was no mass exchange opposition at any current strong fluid or fluid points of interaction, every one of the ensuing examinations was done at a mixing velocity of 2500 fire up/min.

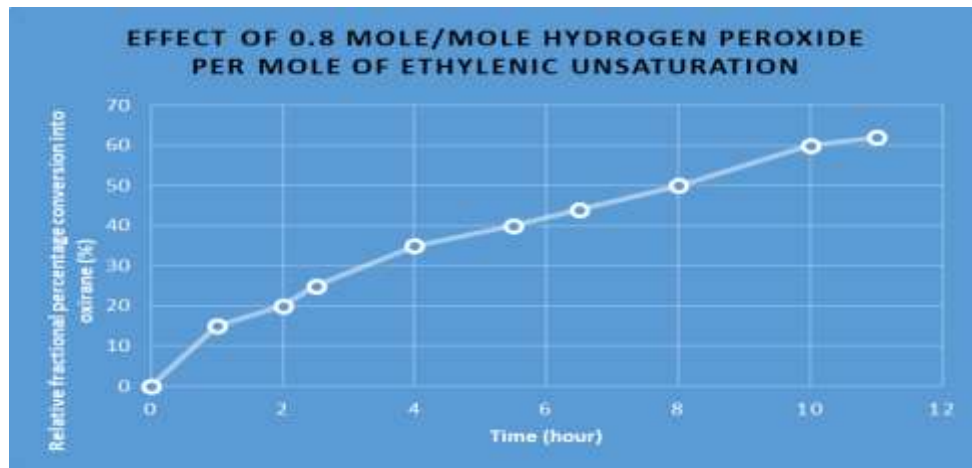### 3.2 Effect of hydrogen peroxide-to-ethylenic unsaturation mole ratio

Table 1: Effect of 0.8 mole/mole hydrogen peroxide per mole of ethylenic unsaturation on relative fractional conversion to oxirane

Time (hour)	Relative fractional percentage conversion into oxirane (%)
0	0
1	11
2	15
3	20
5	25
7	35
9	45
11	55

Figure 2: Graphs for the effect of 0.8 moles of Hydrogen peroxide per mole of Ethylenic unsaturation
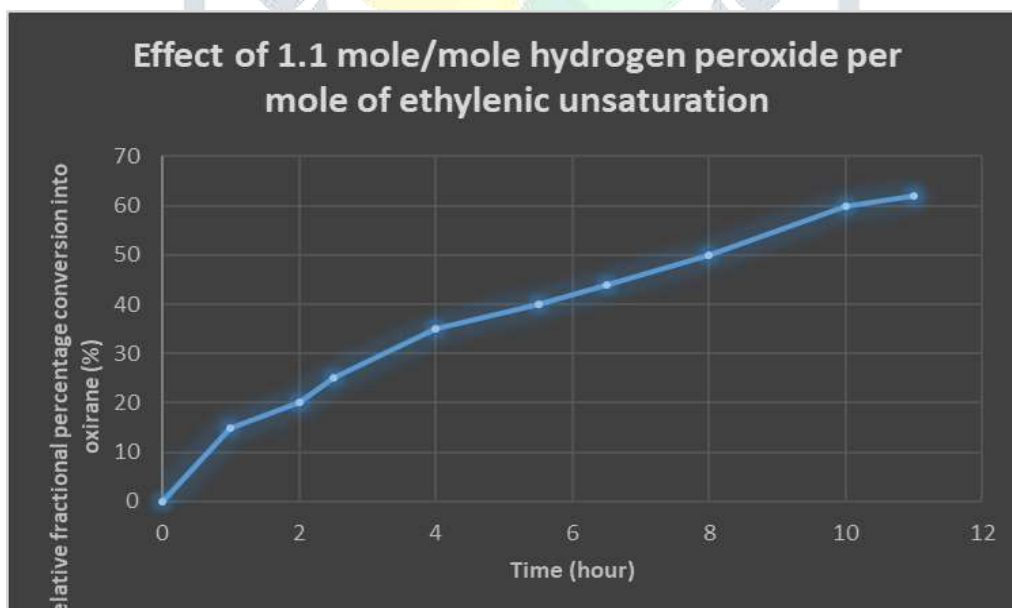
(Source: Self-created in Excel)

The above graph shows the effect of 0.8 moles of Hydrogen peroxide per mole of Ethylenic unsaturation over the fractional conversion to oxirane. The ending point of this graph is 60 percentage on the above 10 hours. The graph is started from the zero point and goes to the upper direction part by part. The graph directed that how time effects the percentage conversion of oxirane. From the graph it can be seen that at 6 hours 45% of the ethylene unsaturation are converted to that of the oxirane. While on the other hnd it can be seen that at 4 hours more than 30 % of the ethylene unsaturation are converted to that of the oxirane. Further it can also been seen that at eight hours about 50 % of the ethylene unsaturation are converted to that of the oxirane. After 10 hours it can be seen that around 60% of the conversion have been mediated to oxirane.

Figure 3: Graphs for the effect of 1.1 moles of Hydrogen peroxide per mole of Ethylenic unsaturation

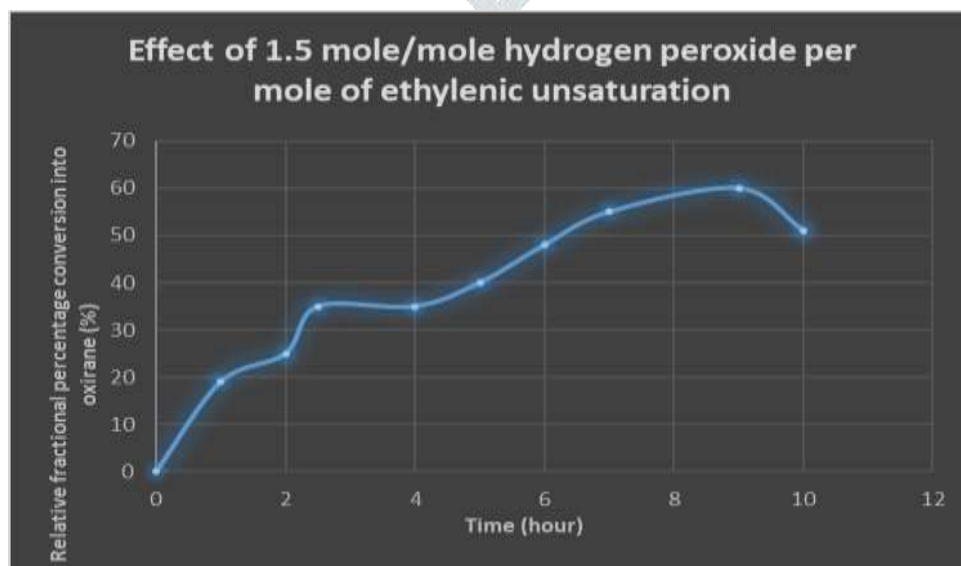(Source: Self-created in Excel)

The above graph shows the effect of 1.1 moles of Hydrogen peroxide per mole of Ethylenic unsaturation over the fractional conversion to oxirane. The graph directed how time affects the percentage conversion of oxirane. From the graph, it can be seen that at 8 hours 50% of the ethylene unsaturation is converted to that of the oxirane. While on the other hand, it can be seen that at 6 hours more than 40 % of the ethylene unsaturation is converted to that oxirane. Further, it can also be seen that at eight hours about 50 % of the ethylene unsaturation is converted to that of the oxirane. After 10 hours it can be seen that around 60% of the conversion has been mediated to oxirane.

Table 2: Effect of 1.5 mole/mole hydrogen peroxide per mole of ethylenic unsaturation on relative fractional conversion to oxirane

| Time (hour)	Relative fractional percentage conversion into oxirane (%)
0	0
1	19
2	25
2.5	35
4	35
5	40
6	48
7	55
9	60
10	51

Figure 4: Graphs for the effect of 1.5 moles of Hydrogen peroxide per mole of Ethylenic unsaturation

(Source: Self-created in Excel)

The above graph shows the effect of 1.5 moles of Hydrogen peroxide per mole of Ethylenic unsaturation over the fractional conversion to oxirane. The graph directed how time affects the percentage conversion of oxirane. From the graph, it can be seen that at 4 hours more than 45% of the ethylene unsaturation are converted to that of the oxirane. While on the other hand it can be seen that at 8 hours more than 55 % of the ethylene unsaturation are converted to that of the oxirane. Further, it can also be seen that at eight hours close to 60 % of the ethylene unsaturation is converted to that of the oxirane. After 10 hours it can be seen that the level of the conversion to oxirane falls to around 50%. In the last section, the graph goes to the downward direction.

Figure 5: Graphs for the effect of 2.5 moles of Hydrogen peroxide per mole of Ethylenic unsaturation
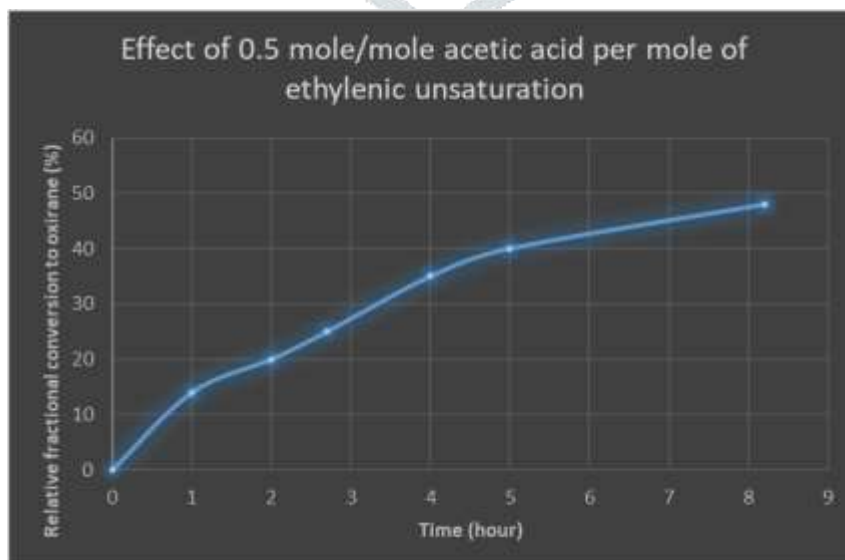
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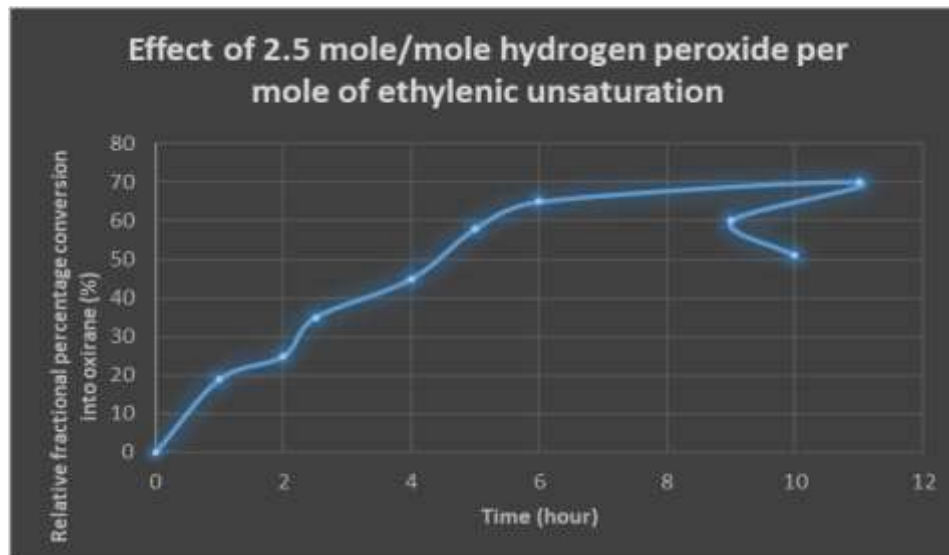
The above graph represents the effect of 2.5 moles of Hydrogen peroxide per mole of Ethylenic unsaturation over the fractional conversion to oxirane. The graph indicated how time affects the percentage conversion of oxirane. From the graph, it can be seen that at 6 hours more than 65% of the ethylene unsaturation is converted to that of the oxirane.

Figure 6: Graphs for the effect of 0.5 moles of Acetic acid per mole of Ethylenic unsaturation

(Source: Self-created in Excel)

The above graph represents the effect of 0.5 moles of acetic acid per mole of Ethylenic unsaturation over the fractional conversion to oxirane. The graph indicated how time affects the percentage conversion of oxirane. From the graph, it can be seen that at 1 hour more than 12% of the ethylene unsaturation is converted to that of the oxirane. While on the other hand, it can be seen that at 5 hours more than 40 % of the ethylene unsaturation is converted to that of the oxirane. Further, it can also be seen that at nine hours close to 50 % of the ethylene unsaturation is converted to that of the oxirane.

3.5 Effect of catalyst loading on the epoxidation rate and on the oxirane ring stability

Table 3: Effect of 5% Amberlite IR-120 loading on relative fractional conversion to oxirane

Time (hour)	Relative fractional conversion to oxirane (%)
0	0
1	9
2	19
2.6	22
4	31
4.5	40
6	47
7	49
8	52
9	52
10	53

Figure 7: Graphs for the effect of 5% Amberlite IR-120 loading on relative fractional conversion to oxirane
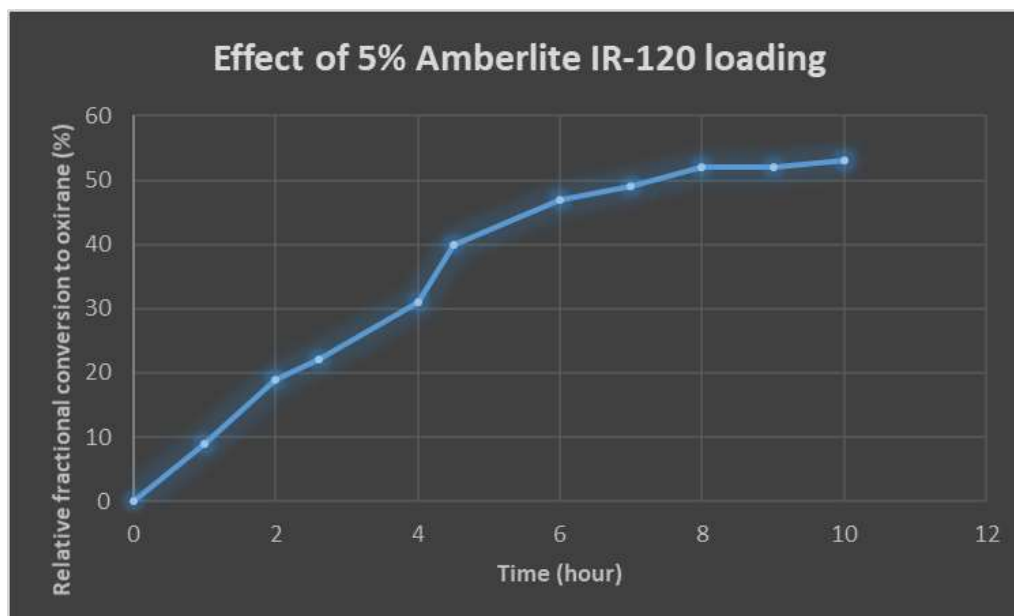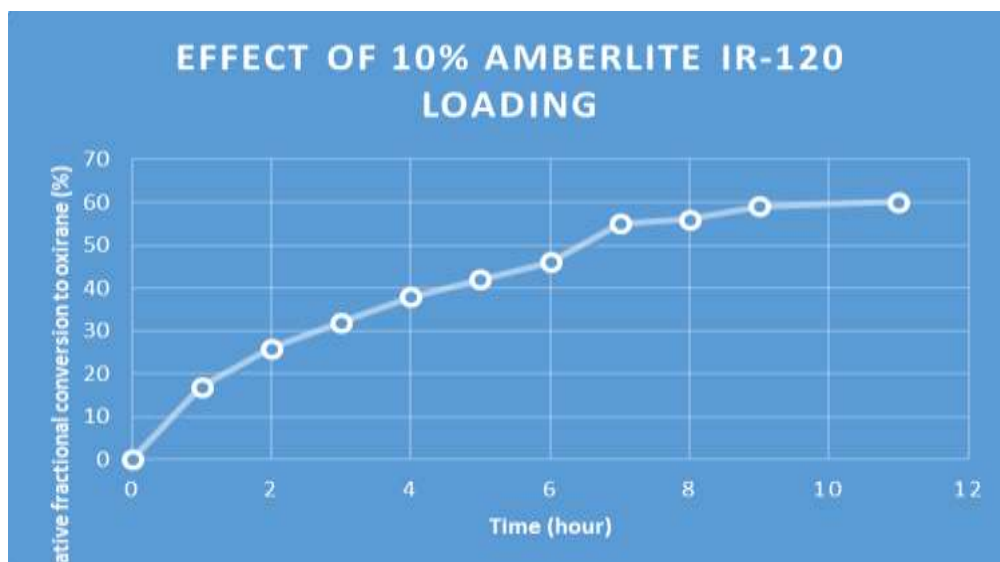
(Source: Self-created)

Table 4: Effect of 10% Amberlite IR-120 loading on relative fractional conversion to oxirane

Time (hour)	Relative fractional conversion to oxirane (%)
0	0
1	17
2	26
3	32
4	38
5	42
6	46
7	55
8	56
9	59
11	60

Figure 8: Graphs for the effect of 10% Amberlite IR-120 loading on relative fractional conversion to oxirane

(Source: Self-created)

The above graph represents the effect of 10% Amberlite IR-120 loading on relative fractional conversion to oxirane. The graph indicated how time affects the percentage conversion of oxirane. The graph shows that at 2 hours more than 20% of the ethylene unsaturation is converted to that of the oxirane.
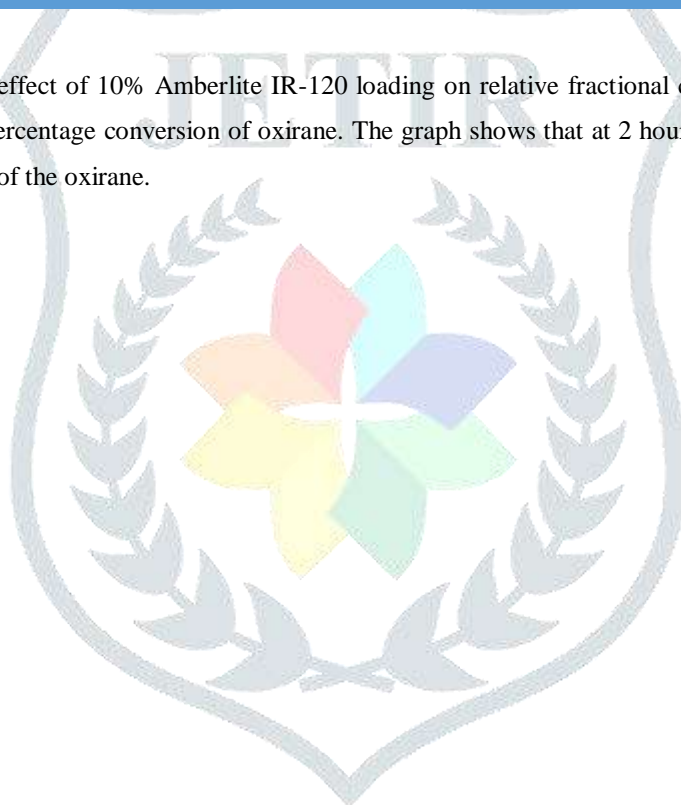
Table 5: Effect of hydrogen peroxide concentration and catalyst (Amberlite IR-120) loading on the iodine value of Jatropha oil

Mole hydrogen peroxide/mole unsaturation								
	0.8		1.1		1.5		2.5	
t(h)	5	10	5	10	5	10	5	10
Conversion of IV (x)	38	58	43	64	50	71	52	89
Glycol, mol/100 gm oil	0.02	0.02	0.02	0.015	0.011	0.013	0.012	0.020
Amberlite IR-120(%)								
	5		10		16		20	
t(h)	5	10	5	10	5	10	5	10
Conversion of IV (x)	39	55	41	63	59	73	58	85
Glycol, mol/100 gm oil	0.01	0.01	0.01	0.017	0.016	0.015	0.011	0.023

Mole acetic acid/mole unsaturation (with toluene)							
	0.3		0.5		0.65		1.0	
T (h)	4.5	9.5	4.5	9.5	4.9	9.5	4.5	9.5
Conversion of IV	44	60	55	75	56	80	64	84
Glycol, mole/100 g oil	0.01	0.01	0.011	0.014	0.012	0.015	0.015	0.021

Table 6: Effect of acetic acid or formic acid concentration (in presence and absence of toluene: the solvent) on iodine value of Jatropha oil

Mole acetic acid/mole unsaturation (without toluene)							
	0.3		0.5		0.65		1.0	
T (h)	4.5	10	5	9.5	5	10	4.9	9.9
Conversion of IV	49	61	55	75	55	79	63	84
Glycol, mole/100 g oil	0.01	0.011	0.011	0.013	0.014	0.018	0.016	0.023

Mole formic acid/mole unsaturation (with toluene)								
	0.3		0.5		0.65		1.0	
T (h)	5	10	5	9.5	4.9	9.8	4.9	9.9
Conversion of IV	50	73	62	82	64	84	65	81
Glycol, mole/100 g oil	0.01	0.0011	0.011	0.016	0.011	0.014	0.013	0.01

Mole formic acid/mole unsaturation (without toluene)								
	0.3		0.5		0.65		1.0	
T (h)	4.5	10	4.5	9.5	5	10	4.9	9.8
Conversion of IV	50	62	57	78	62	82	67	84
Glycol, mole/100 g oil	0.01	0.01	0.011	0.012	0.013	0.016	0.015	0.020

3.7 Determination of the oxygen oxirane content (OOC)

0.3 grams of the sample are weighed and dissolved in 10 milliliters of benzene in a 50-milliliter Erlenmeyer flask. In 100 mL of chilly acidic corrosive, 5 drops of the precious stone violet marker are continuously added to the example arrangement. The titration flagon is covered with an attractively blended elastic plug. While the model plan is blended, it is titrated rapidly with 0.1 N hydrogen bromide reply for a light blue-green endpoint that remained persisted for 30 s and prepared in acidic destructive. By using the equations, theoretical oxirane content value (OOCtheo), experimental oxirane oxygen content value (OOCexp), and finally the relative conversion percentage of oxirane (RCO) can be calculated -

The equation for the calculation of experimental oxirane oxygen content value (OOCexp) -

$OOCexp = V \times N \times 1.60 / Wt$

In the above equation -

OOCexp = experimental oxirane oxygen content value

V = HBr titrant solution's volume

N = Normality of the titrant

Wt = Sample's weight

1.6 = The atomic weight of oxygen divided by the 10

The equation for the calculation of theoretical oxirane content value (OOCtheo) -

$OOCtheo = [(IVo / 2Ai) / 100 + (IVo / 2Ai)] \times (Ao \times 100)$

In the above equation -

OOCexp = theoretical oxirane content value (OOCtheo)

IVo = Initial iodine value

Ao = Oxygen's atomic weight (gmol–1)

Ai = Iodine's atomic weight (gmol–1)

The equation for the calculation of relative conversion percentage of oxirane (RCO) -

RCO = (OOCexp/OOCtheor) x 100

In the above equation -

RCO = relative conversion percentage of oxirane

OOCexp = theoretical oxirane content value (OOCtheo)

OOCtheor = theoretical oxirane content value (OOCtheo)

IV. CONCLUSION

Jatropha oil is a non-consumable vegetable oil that is ordinarily utilized as a feedstock for biodiesel creation because of its high oil content and potential as a maintainable option in contrast to petroleum derivatives. One of the most widely recognized ways of changing over jatropha oil to biodiesel is by an interaction called transesterification, which includes responding the oil with a liquor (generally methanol) and an impetus (like sodium or potassium hydroxide) to deliver unsaturated fat methyl esters (FAMEs).Epoxidation is a compound response that changes over unsaturated fats into their relating epoxides, which are more steady and impervious to oxidative debasement.

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