RESEARCH ARTICLE OPEN ACCESS

Optimum Operating Conditions for Epoxidation Reaction of Jojoba and Castor Oils

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ABSTRACT
The goal of this paper is to determine the best set of parameters such as, glacial acetic acid to ethylenic unsaturation mole ratio (acid/ethylene), hydrogen peroxide to ethylenic unsaturation mole ratio (H_2O_2/ethylene) and temperature on epoxidation conversion based on experimental results, with respect to time. The effect of these parameters has been studied in a separate set of experiments. Their ranges were as follows: 0.2-0.8Wt%, 0.75-3Wt%, and 40^{o}C-80^{o}C respectively. Six models have been introduced to indicate the effect of these three variables on conversion for both jojoba and castor oil, and the prediction abilities of the resultant models were tested. Regression analysis is used to extract the introduced non linear models. In addition, two new correlations have been introduced to incorporate all the studied variables and their effect on conversion simultaneously for both jojoba and castor oil. An optimization program has been introduced to determine the optimum operating conditions for maximum conversion for both jojoba and castor oil. The study shows that, the maximum conversion for epoxidized jojoba oil (66%) could be achieved at acid/ethylene ratio: 0.4, H_2O_2/ethylene ratio: 1.44; temp: 66.5 and time is 8hr. While the maximum conversion for epoxidized castor oil (53.24%) could be achieved at acid/ethylene ratio: 0.37; H_2O_2/ethylenes ratio: 1.32; temp: 61 and time is 8hr. the model results are strongly agreed with the experimental results.
KEYWORDS- Acetic acid, Castor Oil**;** Epoxidation Reaction; Jojoba Oil; Optimization

I. INTRODUCTION

The use of vegetable oils and animal fats for lubrication purposes has been practiced for many years as an alternative to mineral oil as lubricant base stocks [1, 2]. The vegetable oil-based lubricants may be derived from rapeseed oil, cotton seeds, soybean oil, sunflower seed oil, corn oil, palm oil, coconut oil, and peanut oils. Common vegetable oils consist of long chain fatty acids, which contain a combination of saturated and unsaturated with double bond fatty acids. Oils containing mostly saturated fatty acids will have better oxidative stability compared to oils with predominantly unsaturated fatty acids, for example, oleic acid [3,4]. Unsaturated double bonds in the fatty acids are active sites for many reactions, including oxidation which lowers the oxidative stability of vegetable oils [5]. Oxidation is the single most important reaction of oils resulting in increased acidity, corrosion, viscosity, and volatility when used as lubricant base oils [6].

The iodine value (IV) is a measure of the number of double bonds, while the oxirane value (EPO) is an indication of the percentage content (%, by wt) of epoxide oxygen. The quality of the epoxidized oil is better; the higher the oxirane value and the lower the iodine number [7–9]. Several processes are available for the preparation of epoxidized oils. The most widely used process is the epoxidation of unsaturated compounds with either pre- or *in-situ*-formed organic per acids. *In-situ* epoxidation using hydrogen peroxide with either acetic or formic acid as the per oxygen carrier has achieved commercial importance [10–13]. Epoxidation reaction results of some vegetable oils indicate that the net yield of epoxides is determined by rates of both reactions, which depend on several factors, such as organic acid concentration and reaction temperature [14, 15]. The formation of oxirane ring is affected by several factors, namely concentration of glacial acetic acid, concentration of hydrogen peroxide, temperature, and reaction time. In this work, six models have been introduced to indicate the effect of these factors on conversion for both jojoba and castor oil, and the prediction abilities of the resultant models were tested. Regression analysis was used to extract the introduced models [17]. Two additional models incorporate all affecting parameters simultaneously on conversion within the valid operating conditions for both jojoba and castor oil. Also, an optimization program has been introduced to determine the optimum operating conditions for maximum conversion of epoxidation reaction for both jojoba and castor oil.

II. EXPERIMENTAL

2.1. Procedure of Epoxidized Jojoba and Castor Oils

As previously reported [16], epoxidation reaction of jojoba and castor oils were carried out; Peracetic acid which was prepared in-situ by reacting various ratios of glacial acetic acid and hydrogen peroxide in the presence of 3%wt of concentrated sulphuric acid. The obtained optimum conditions of this study, temperature, molar ratio of hydrogen peroxide to unsaturation bond and ratio of acetic acid to unsaturation bond were 60^{o}C, 1.5:1, and 0.4:1 respectively.

In this section, the effects of the independent variables (acid/ethylene, H_2O_2/ethylene and temp, on conversion were studied. Their ranges were as follows: acetic acid to ethylenic unsaturation mole ratio 0.2-0.8, hydrogen peroxide to ethylenic unsaturation mole ratio 0.75-3, and temperature 40-80C. All the experiments were carried out at stirring speed 800 rpm and time observation from 1 to 8 hours. When the effect of acetic acid to ethylenic unsaturation mole ratio was studied, the temperature is kept at 60^{o}C while the hydrogen peroxide ratio is 1.5 (Model 1). When the effect of hydrogen peroxide ratio was studied, the acetic acid was 0.4 while the temperature was kept as 70 ^{o}C. The effect of temperature was studied at acetic acid 0.4 mole and hydrogen peroxide 1.5 mol (Model 2). Temperature effect on epoxidation reaction was investigated at the acetic acid to ethylenic unsaturation mole 0.4 and hydrogen peroxide to ethylenic unsaturation mole ratio 1.5 (Model 3).

Comparison of model predictions with experimental results of epoxidation reaction of jojoba and castor oils were obtained through applying regression analysis using Excel program [17]. The statistical analysis was then carried out to solve nonlinear programs to determine global optimum solution for maximum values of epoxidation conversion reaction of oil under investigation.

In this respect, Lingo software version 14 was applied to study the effects of the above mentioned affecting parameters at different times; a parity plot is used to compare between experimental with predicted values for conversion of jojoba and castor oil. Besides that, the surface response plots were developed and used to determine effect of different operating conditions on conversion for both epoxidized jojoba and castor oils Fig. "3a, b, c & 4a, b, c"

NOTATION: A, acetic acid to ethylene ratio; H, is hydrogen peroxide to ethylene ratio; S, time; T, temperature

Conversion = -13.9147+79.42345*A + 7.822177*S - 160.756*A^3 - 0.20981 * S^2 1.98822 * A^2* S + 9.424398 *A * S-.63587*S^2* A (1)

Conversion = -53.6152 + 6.735268* S + 112.7283* H – 67.3663 * H2+ 11.6642 * H3 + 3.959762 * H * S -0.14092 * S2 -0.1316 * H (2)

Conversion =157.1752 - 43.3552 * S - 6.39283 * T + 0.089709 * T^2 - 0.00044 * T^3 + 1.335781* T * S – 0.00638 * T^2 * S + 3.6475 * S^2- 0.07304 * S^2 * T (3)

R-Squared statistics for the develop models of acid ratio, H_2O_2 ratio and temperature are indicated in "Table 1".

III. Result and discussion

3.1. Effect of acid/ethylene, H_2O_2/ethylenes and temp on conversion for jojoba oil epoxidation reaction

The epoxidation reaction for oils under investigation was carried out at different operating conditions; acid/ethylene ratio, H_2O_2 ratio, temperature and time as previously reported [16]. Epoxidation conversion at these conditions was used to extract a good correlation behavior through regression analysis of these experimental data.

Through studying the behavior of conversion with the different operating conditions, it is found that the conversion is quadratic dependent on H_2O_2 ratio, temperature and time. While it is found that the best fitting of conversion with acetic acid to ethylene ratio is cubic relation. Depending on these results, different correlations, or models, could be generated through regression analysis of experimental data.

Table 1: R^2 Statics for Jojoba Oil Models

Model	R^2	Adjusted R^2	Standard error
Model 1	0.9949	0.9153	1.5612
Model 2	0.9528	0.9391	4.9143
Model 3	0.9133	0.8909	5.5182

3.2. Effect of acid/ethylene, H_2O_2 /ethylene and temp on conversion for castor oil epoxidation reaction

The regression analysis of experimental data generated the following equation:

Conversion = -25.9603 + 165.9304 * A + 15.2381* S - 294.782 * A^2 + 165.964 * A^3-.98294 * S^2 - 4.0625 *A^2 *S-4.9003 * A * S + .587798 * S^2 *A (4)

Conversion = -20.9089+ 10.08888* S + 49.11467 * H - 30.5798 * H^2 + 5.402469 * H^3 +

$2.002914 * H * S - 0.58739 * S^2 - 0.0801* H^2 * S^2$ (5)

Conversion $=19.63464 - 9.0719* S - 0.1441* T - 0.00948 * T^2 + 0.00011 * T^3 + 10.621768* T * S - 0.00386* T^2 * S + 0.339286* S^2 - 0.02349 * S^2 * T$ (6)

R-Squared statistics for the develop models of acid ratio, H_2O_2 ratio and temperature are indicated in "Table 2".

Table 2: R^2 Statics for Castor Oil Models

Model	R^2	Adjusted R^2	Standard error
Model 1	0.9849	0. 9774	2.1113
Model 2	0.9490	0. 9342	3.6533
Model 3	0. 9425	0. 9276	3.0017

The R^2 statistical test was used to evaluate how well the experimental data were represented by the correlations. R^2 is a value that always falls between 0 and 1. It is the relative predictive power of a model, [18]. The closer R^2 up to 1 gives the better model representing the experimental data, [19]. This value for all the introduced correlations was found to be within the range (0.91 to 1). The equations are valid within the operating conditions studied.

Multiple regression analysis of the experimental data was generated quadratic polynomial equation, which represented epoxidation of both oils conversion by Equations from 1to 6. "Tables 3 and 4" indicate a comparison between the experimental and predicted conversion of epoxidation reaction for each of the three models extracted for both jojoba and castor oils respectively; where **Model 1** corresponds to the effect of both acetic acid to ethylene unsaturated and time on conversion; **Model 2** corresponds to the effect of both hydrogen peroxide ratio and time on conversion; **Model 3** corresponds to the effect of temperature on conversion at different times.

"Fig. 1 and 2", represented the parity plot including the experimental and predicted value of epoxidiesed conversion for jojoba and castor oils, respectively .

Table 3: Comparison between experimental and predicted conversion values for jojoba oil epoxidation reaction

Model 1		Model 2		Model 3	
Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
9.5	9.974451	10	7.448472	12	14.26083
10.8	11.18569	13	6.681667	18	19.38376
18	18.59103	14	10.49556	22	21.56973
20	18.3759	15	15.50764	23	22.88883
22	22.17276	23	19.90488	26	29.04255
26	26.53364	25	25.13905	26.5	25.89719
28.5	28.25726	30	31.51375	28.5	29.71616
31	31.97716	35	37.36119	30	27.84604
35	37.21029	35.8	41.50827	36	36.5068
36	33.80229	42	41.11002	42	43.96248
41.5	40.39697	43.8	46.97687	43.2	45.09481
42.5	40.59891	50	48.45065	45	42.11689
45.4	45.23502	51.5	49.88845	46	51.98556
48.5	48.038	55	55.71847	49.3	49.9518
49	51.56442	57.5	56.65429	50	51.40959
51.9	52.33143	58	55.36139	51.7	51.43053
57	56.1372	59.2	61.84222	58.9	58.33027
59	59.36819	62.4	57.18048	61.2	58.46745
62.6	63.73931	62.8	61.80577	61.4	57.74311
62.8	63.2593	65.6	53.14496	62	58.84813
69.8	68.05079	75	76.69889	63.6	66.2781

Table 4: Comparison between experimental and predicted conversion values for castor oil epoxidation reaction

Model 1		Model 2		Model 3	
Experimental	**Predicted**	**Experimental**	**Predicted**	**Experimental**	**Predicted**
7	9.992361	10	11.96373	12.5	14.78345
13	13.52986	12	11.87308	13.6	14.04994
16	15.74861	16	14.51754	15	13.95988
22	22.4745	20	21.54579	16	15.17577
26.3	26.13313	22.4	21.65745	26.3	26.78256
31	30.15863	26.3	25.30796	29.2	29.68512
33	31.26042	29.7	33.60228	33	32.08411
36.9	35.02202	30.7	30.08628	35	34.05107
38	36.58224	35.4	37.25022	36.9	35.77875
39	39	36.9	34.56317	39	38.84345
40	41.74534	42	42.28316	39.8	41.60077
40.2	39.29831	43.4	42.13635	40	40.8856
42	42.41528	44	46.57225	42	43.43494
43.4	45.60546	46	48.15543	44	43.66774
45	45.64792	47.8	47.7834	44.5	43.09369
46	48.3129	49	49.54571	46	45.93935
47.6	49.67153	50.3	49.84345	47	47.92994
49	50.18185	53	53.257	48	48.10244
53.8	54.14236	55	51.15265	48.3	37.92964
54.4	53.02748	57.5	56.23182	51.2	46.81655
58.3	57.03194	57.6	57.81093	52	48.54488

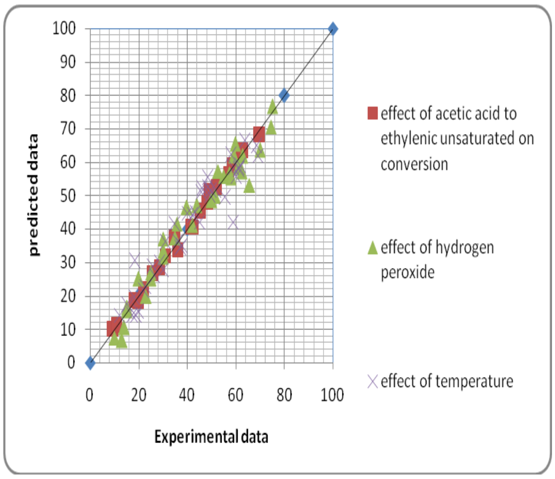

Figure (1): Parity plot for different introduced models for jojoba oil

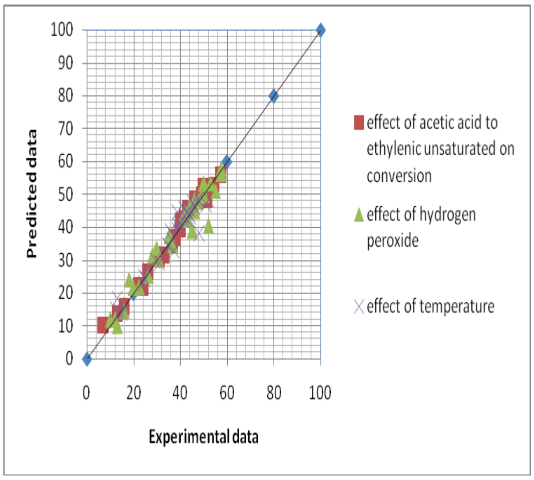

Figure (2): Parity plot for different introduced models for castor oil

It could be observed from "Tables 1&2" and from parity plots that there is excellent agreement between models predicted values and experimental data within the range of conditions used to develop the models. The plotted data points obtained by the new correlations are quite close to the perfect correlations of the 45^{o} line. This shows that the correlations are able to predict conversion at different operating conditions.

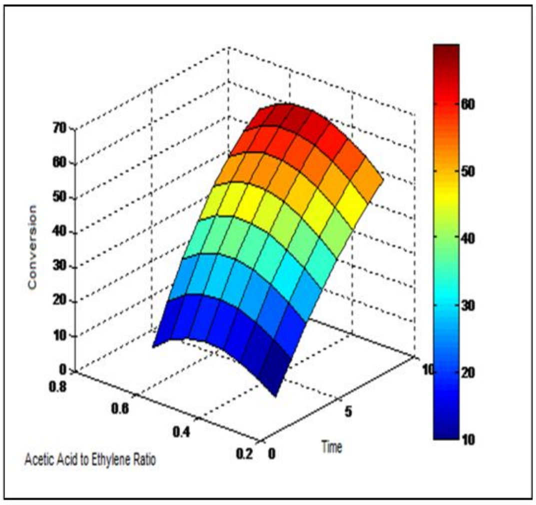

Figure 3a: Surface plot of epoxidation conversion as a function of glacial acetic acid to unsaturation ethylene ratio and time at constant temperature and hydrogen peroxide and temperature of jojoba oil

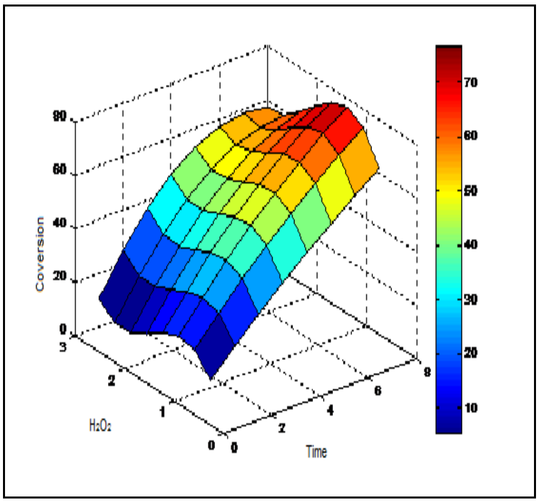

Figure 3b: Surface plot of epoxidation conversion as a function of hydrogen peroxide ratio and time at constant temperature and glacial acetic acid to unsaturation ethylene ratio of jojoba oil

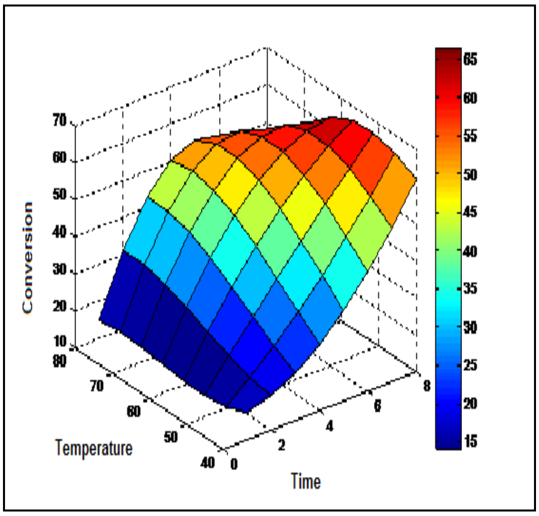

Figure 3c: Surface plot of epoxidation conversion as a function of temperature and time at constant both hydrogen peroxide and glacial acetic acid to unsaturation ethylene ratio of jojoba oil

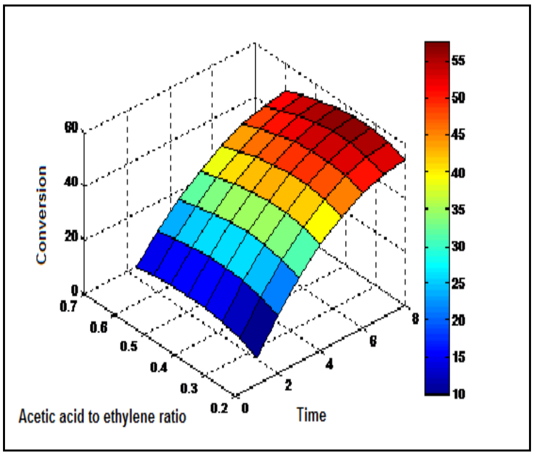

Figure 4a: Surface plot of epoxidation conversion as a function of hydrogen peroxide to unsaturation ethylene ratio and time at constant hydrogen peroxide and temperature of castor oil

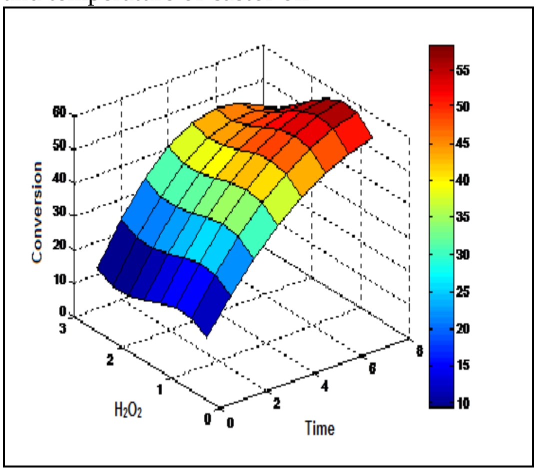

Figure 4b: Surface plot of epoxidation conversion as a function of hydrogen peroxide ratio and time at constant glacial acetic acid of castor oil

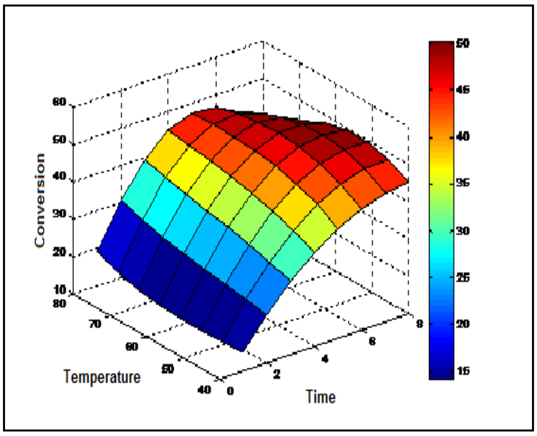

Figure 4c: Surface plot of epoxidation conversion as a function of temperature and time at constant hydrogen peroxide and glacial acetic acid of castor oil

Fig " 3 and 4" are three-dimensional plots represent the surface response of epoxidation conversion through varying glacial acetic acid to ethylene ratio, hydrogen peroxide, temperature and time for both jojoba and castor oils respectively. The contour plots can be used to characterize the shape of the surface and locate the optimum response, approximately, by varying two variables within the experimental range and holding the other one constant. The glacial acetic acid concentration has a negative effect on percentage of conversion in a linear term as well as in the quadratic terms. This is most likely due to the degradation of oxirane ring by the glacial acetic acid, which participates in the reaction in two capacities: first, as the catalyst in formation of oxirane ring and second, as a reactant in the hydrolysis of oxirane ring into hydrogen group [20]. These figures reveal that the epoxidation reaction of both oils under investigation could take place at lower temperature, but yield a more stable oxirane ring. The optimum rate of epoxidation will be at moderate temperature 66 ^{o}C and take place in time 7 hour.

3.3. Effect of All Operating Conditions Simultaneously on Conversion for Both Jojoba and Castor Oil

A new and very important model has been introduced to incorporate all the studied variables and their effect on conversion simultaneously in one correlation. This correlation could predict first: the conversion based on any value for the operating conditions. Second: the optimum operating conditions those give the maximum conversion. Accordingly, the correlation has been extracted and illustrated as follows:

3.3.1. For Jojoba Oil:

$$\text{Conversion} = -21.0618 + 92.84734 * A + 12.7636 * \mathbf{S} + 105.9733 * H - 5.32186 * T - .65454 * S^2 - 56.9263 * H^2 + .116843 * T^2 - 151.355 * A^3 + 9.364885 * H^3 - .00077 * T^3 \quad (7)$$

3.3.2. For Castor Oil:

$$\text{Conversion} = 59.8814 + 26.48006 * A - 6.13509 * \mathbf{S} + 34.5649 * H - 3.81937 * T - 13.7821 * A^2 - 0.94137 * S^2 - 19.3939 * H^2 + 0.052012 * T^2 - 39.8761 * A^3 + 3.197755 * H^3 - 0.0002 * T^3 + 0.703918 * T * S - 0.00609 * T^2 * S \quad (8)$$

Lingo software version 14 and statistical analysis are useful tools to optimize the different operating conditions of epoxidation reaction for jojoba and castor oils. An optimization program constructed based on the above correlation, could be formulated as follows:

$$\text{Maximize Conversion} \quad (9)$$

Constraints for upper and lower bounds of each affecting variable are formulated as follows

$$A^L \geq A \geq A^U \quad (10)$$
$$S^L \geq S \geq S^U \quad (11)$$
$$H^L \geq H \geq H^U \quad (12)$$
$$T^L \geq T \geq T^U \quad (13)$$

Equations (9-13) form a non-linear program (NLP) aims to introduce the preferred operating conditions for maximum epoxidation reaction conversion, for either jojoba or castor oils. Equations (10-13) represent the limitation for the operating variables, in which the introduced conversion model is valid. Lingo software is an optimization program capable of solving such model to get the global optimum solution. The solution of that program for jojoba oil indicates that the total number of variables is 5; four of them are nonlinear variables. It suggests that the maximum conversion could be achieved is 66% at acetic acid ratio of 0.452, time of 8hr, hydrogen peroxide ratio of 1.44 and temperature of 66C. While the maximum conversion for castor oil is 53.24%, which could be achieved at acetic acid ratio of 0.37, time of 7.5hr, hydrogen peroxide ratio of 1.32 and temperature of 61C. These obtained results are greatly matched to the experimental results, which are achieved in a series of exhausting consecutive experiments. It is recommended to use the introduced models for knowing conversion at any operating conditions at the valid range of operating conditions, or knowing the optimum operating conditions for maximum conversion, rather than doing experimental work. The reason is that experiments are carried out over a distinct limited number of points, while the introduced models enable the user to study the whole period of operating conditions rather than the high number of experiments iterations.

IV. CONCLUSIONS

The suitability of the model equation for predicting the optimum response value can be tested using the defined optimum conditions. Based on the experimental data, the optimum operation condition and response value could be predicted and estimated by using Lingo software version 14 and applying regression analysis using Excel program. The maximum conversion for epoxidized jojoba oil (66%) could be achieved at acid/ethylene ratio: 0.4;, H_2O_2/ethylenes ratio: 1.44; temp: 66.5 and time is 8hr. while the maximum conversion for epoxidized castor oil (53.24%) could be achieved at acid/ethylene ratio: 0.37; H_2O_2/ethylenes ratio: 1.32; temp: 61 and time is 8hour. So, the model results were strongly agreed with the experimental results.

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