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Synthetic epoxidation of *Moringa oleifera* Lam with performic acid generated *in situ*

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ABSTRACT

In this work a synthetic process applied for the epoxidation of moringa oil (*Moringa oleifera* Lam) with performic acid generated *insitu* was studied. For this,it was used the fractional factorial design of two levels 2^{4-1}, which investigate temperature, reaction time, the acid ratio,as well as hydrogen peroxide and formic content. The selectivity, kinetics and thermodynamics for this reaction was also analyzed at epoxy temperature range (30 °C to 70 °C). The results showed that for the epoxidation of oil are required a 3 hour reaction, 30 °C and a ratio H_2O_2/C = C/HCOOH (1.5: 1: 1), with the final conversion value equal to 91.02 % (± 0.4). The approach applied afterwards was effective for optimizing the epoxide synthesis conditions. This synthetic derivative obtained in this study has potential use in the manufacture of chemicals, in particular lubricants, additives, polymers and biofuels.

Keywords: *Moringa oleifera Lam, fractional factorial design, epoxidation, synthetic optimization process.*

1. INTRODUCTION

Making the transition from petroleum to renewable resources is important for sustainable development because of the depletion of oil reserves, global warming and other environmental problems. Fats and oils derived from plants have high potential for use in the petrochemical industry because they are biodegradable and sustainable and can be converted into various industrial products. Specifically, epoxidized vegetable oils are widely used as lubricants, plasticisers, and polymer stabilizers paint components and environmentally friendly coatings. Additionally, they serve as intermediates for various chemicals, including alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds and polymers such as polyesters, polyurethanes and epoxy resins [1-5].

The epoxidation of vegetable oils can be implemented by various methods such as the conventional method (Prileshajev-epoxidation), catalytic epoxidation using an acidic ion exchange resin (AIER), chemical and enzymatic epoxidation and also and metal-catalyzed epoxidation. Among them, the conventional method is most widely used and cost-effective for epoxidation in which hydrogen peroxide is used as an oxygen donor and carboxylic acid (e.g. formic acid, acetic acid) that act as the active oxygen carrier, as well as catalyst. In some cases a small amount of inorganic acid (e.g., HCl, H_2SO_4, HNO_3, H_3PO_4) is also added to further catalyze the process [6-12].

In order to optimize chemical characteristic of the oxiranic ring resulting from epoxidation of carboxylic acids, evaluation of the kinetic and thermodynamic behavior, oxidizing approach and also development of factorial statistical experimental design, have been developed [13-21].

In the concern ofthe epoxide synthetic study of oleic acid, one of the main fatty acids present in Moringa oleifera Lam oil, it was evidenced that the degradation of the oxirane ring is influenced by the amount of the catalyst agent (sulfuric acid) and also by the hexane addition time during the reaction process [22]. In that work, oil epoxidation was obtained in the presence of acetic acid, hydrogen peroxide, sulfuric acid and an organic solvent (hexane). In this condition, reaction rates increase with sulfuric acid amount, but this catalyst agent causes oxirane ring degradation, reducing the epoxide production. Additionally, it was observed that the best value obtained for the catalyst was 3.5%, with epoxide yield higher than 90%, in which reaction occurred at 50 °C to 55 °C for 5 hours, under speed condition (1200 rpm) and specific molar ratio of oleic acid:acetic acid:hydrogen peroxide (1:0.4:1.5). This experimental approach resulted in an oxirane oxygen and iodine value equal to 3.15 and 4.66, respectively. It was proved that the addition of hexane did not influence the reaction rate of cleavage of the double bond. Otherwise, hexane over addition time contributes to the degradation of oxirane rings already formed.

A patent developed by Gall and Greenspan [23] reports another efficient method for oleic acid epoxidation. In which, hydrogen peroxide and formic acid (0.25:1 of molar ratio) in the presence of an organic solvent (benzene or hexane) at relatively higher temperature (50 °C to 100 °C), 1 to 5 hour reaction, afforded maximum epoxy conversion (90%).

Moringa oleifera is commonly called in some parts of the world horseradish tree and drumstick tree, among other denominations such as kelor tree, mother's best friend, west Indian ben, shagara al Rauwaq and sohanjna. Specifically, in Brazil, M. oleifera is commonly known as lírio-branco, quiabo-de-quina and moringa.Its seeds contain 85% of unsaturated fatty acids in which oleic acid corresponding to 79% [24-26].

Furthermore, recent studies by Silva et al. [27, 28] proved the great potential of using epoxidized passion fruit and moringa oils without the addition of solvent and catalyst applied to hydraulic systems. The lubrication performance of these new

fluids showed superior results of lubrication and physico-chemical characteristics compared with conventional hydraulic mineral based lubricants. In this present study the oil epoxy synthesis of *Moringa oleifera* was optimized in a selectivity study conducted by 2^{4-1} fractional factorial design, kinetic and thermodynamic analyzes aiming at efficient carboxylic acids to epoxy transformation to produce great amount of semisynthetic product.The epoxy conversion process was conducted in the presence of performic acid, generated *in situ*, as a reaction medium.

2. EXPERIMENTAL SECTION

2.1. Materials.

Moringa oleifera Lam oil was extracted by cold pressing, resulting in a satisfactory extraction amount of 40%. In addition, sources of other chemicals were supplied by a different company and used as received, as follows: Chloro iodine sec. Wijs, formic acid (85.0%), sodium thiosulfate (99.5%), potassium iodate (99.0%) and anhydrous sodium carbonate (99.0%) supplied by Mahal Impex Comercial Ltda. Anhydrous sodium sulfate (99.0%) and toluene (99.5%) by Vetec. Chloroform (99.0%) by Quimex Chemical Products Ltda., Brazil. Cyclohexane (99.5%) and hydrogen peroxide (30.0%) by Labsynth Products Laboratory Ltda., Brazil.

2.2. Experimental design for fractional factorial 2^{4-1}.

In the experimental work of the epoxide synthesis applied for moringa oil (*M. oleifera*) a mathematical model was applied involving four factors, two-level 2^{4-1} fractional factorial design according to a previously reported methodology. [29,30]. For that, variables such as time (A), temperature (B), ratio of the catalyst formic acid (C) and hydrogen peroxide (D) were analyzed. Table 1 presents values of the investigated experimental domains (variables and their levels) for the epoxy conversion.

Table 1. Values of the investigated experimental domains (variables and their levels) in the epoxidation of moringa oil (M. oleifera).

Factor	Unit	Level	
		Minimum	Maximum
A	H	(-) 2	(+) 5
B	°C	(-) 50	(+) 90
C	mol/mol	(-) 0,3	(+) 1
D	mol/mol	(-) 0,5	(+) 1.5

Software Statistica 7.0 was applied for data treatment and also to provide statistical charts. The results of iodine value (IV) and oxirane oxygen (OO) were used to research synthetic optimized conditions as well to evaluate surface curves.

2.3. Experimental Setup.

In a 250 mL flask attached to a reflux condenser, under constant heating and agitation (500 rpm), moringa oil was added, followed by formic acid and hydrogen peroxide, under proportions and conditions established by fractional factorial design 24-1 study. To avoid hydrolysis of the vegetable oils, hydrogen peroxide was added fractionally during the first hour of reaction process.

2.4. Analytical Techniques.

2.4.1. Iodine Value (IV).

Iodine value was determined according to Wijs method [31] in which the iodine value (IV) is defined as a measure of the degree of the fatty acids unsaturations present in the oils and fats. This value is expressed as the weight of iodine absorbed per 100 g of sample.

2.4.2. Oxirane oxygen (OO).

The percentage of the oxirane oxygen was determined by direct method established by IUPAC [32] using hydrobromic acid solution in glacial acetic acid. The content oxirane oxygen (OO) was calculated according to the consumed amount of the halogen atom.

2.4.3. Hydrogen Nuclear Magnetic Resonance (^{1}H NMR).

The ^{1}H NMR spectrums of the oil sample and their respective semisynthetic epoxide reaction product were obtained on a Bruker AVANCE® 200 NMR spectrometer, operated at 200 MHz for ^{1}H NMR. Deuterated chloroform was used [standard tetrametilsilano (TMS) as solvent, at ambient temperature]. Samples were prepared at a concentration of approximately 0.25 mg/mL.

3. RESULTS SECTION

The epoxidation synthesis of the oil obtained from *Moringa oleifera* Lam, involved in the first stage of the characterization of the vegetable oil, followed by kinetic and thermodynamic investigations of the epoxidation process. As preliminary results, the observed iodine value (g I_2/100 g) was 71.91 for *M. oleifera* and for oxirane oxygen the value was zero.

3.1. Design and optimization experiments.

The fixed ratio for formic acid (0.65:1) and hydrogen peroxide (1:1) obeying the applied mathematical model for IV and OO, resulted in the response surfaces, as represented in Figure 1.Through the analysis of the response surfaces shown in the Figure. 1a and 1b, it is observed that the best conditions (65%) for the EMO synthesis is 5.5 hour reaction, 55 °C, predicting IV around 10.00 g I_2/100 g and an OO of 2.80%.

However, by changing the values of the ratio of hydrogen peroxide (1.5:1) and formic acid (1:1), the new response surfaces (Figure. 1c and 1d) increase EMO yield reaching values greater than 95%, while decrease IV and increase OO, being necessary at least 2 hours of reaction at 50 °C.

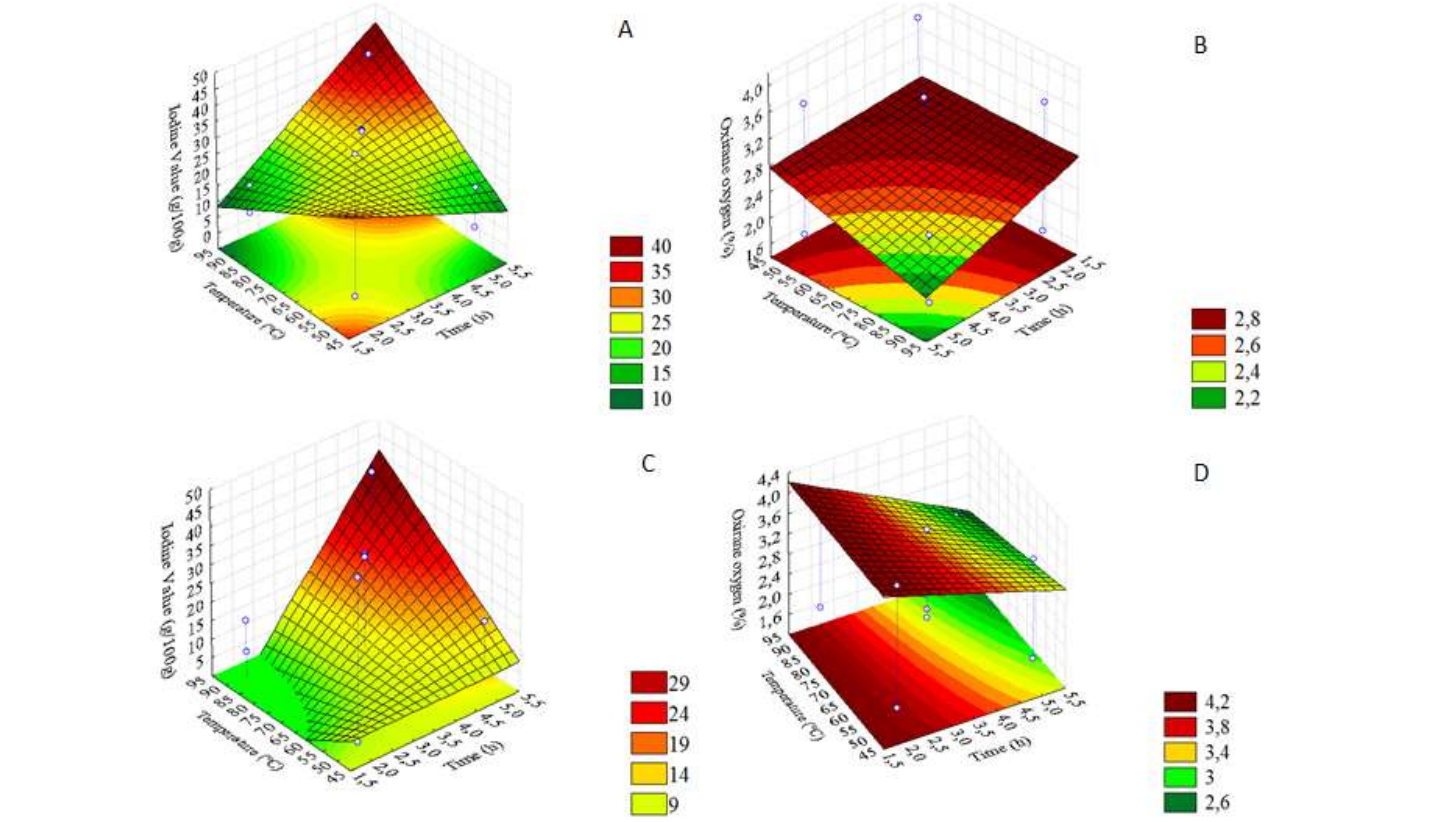

Figure 1. (a) Surface Response of the EMO as a function of IV; (b) Surface Response of the EMO as a function of OO; (c) Surface Response of the EMO as a function of IV; (d) Surface Response of the EMO as a function of OO.

The mathematical model for the IV and OO of the EMO was obtained by linear regression, as shown in Eqs. (1) and (2), respectively.

$$Y_{IV[EMO]} = 143.82(\pm0.10) - 28.13\,[t](\pm012) - 0.91\,[T](\pm0.11) - 42.25\,[CH_2O_2](\pm0.11) - 35.33[H_2O_2](\pm0.11) + 0.28[t][T](\pm0.11) + 8.48\,[t][CH_2O_2](\pm0.11) + 4.59\,[t][H_2O_2](\pm0.11) \quad (1)$$

$$Y_{OO[EMO]} = -0.37\,(\pm0.28) + 0.53[t](\pm0.03) + 0.005[T](\pm0.03) + 5.64[CH_2O_2](\pm0.03) - 0.61[H_2O_2](\pm0.03) - 0.003[t][T](\pm0.03) - 1.26[t][CH_2O_2](\pm0.33) + 0.42\,[t][H_2O_2](\pm0.03) \quad (2)$$

The optimal experimental conditions suggested by analysis of the graphs of response surfaces for epoxidation of moringa (Figure 1c and 1d) were verified by assay in triplicate and by IV and OO results, as shown in Table 3.

The results presented in Table 2 demonstrate that the graph of the surface response is representative for the optimization of the epoxidation of EPO as well as EMO in the presence of performic acid generated in situ.

Table 2. Final Characterization of the oil and the epoxides of moringa.

Analysis	Oil	Epoxide
Iodine Value (g I_2 / 100g)	71.90 (±0.25)	6.18 (±0.31)
Oxirane Oxygen (%)	-	4.08 (±0.23)
Conversion according to the IV	-	91.40 (±0.4)

3.2. Hydrogen Nuclear Magnetic Resonance (^{1}H NMR).

After syntheses optimization, the technique of Nuclear Magnetic Resonance (^{1}H NMR) was used to investigate the chemical structure of the epoxides compounds. The epoxidized moringa oil (EMO) revealed the absence of the signal at approximately 5.3 ppm, corresponding to HC=CH unsaturation signal present in the target oil (this absorption was observed in the ^{1}H NMR before epoxy formation). After the reaction process, signal near 3.1 ppm, was associated to the hydrogens attached to carbons connected with the epoxy cycle. It was also possible to confirm that the allylic hydrogens of carbons sp^2 suffered a shift of about 2 ppm to 1.5 ppm. It can be considered that this shift is also a consequence of the influence of the oxygens of the epoxy group [33, 34, 35].

3.3. Kinetics.

For an optimal reaction condition assays were performed in duplicate to investigate the reaction kinetics at 30 °C, 50 °C and 70 °C. The reaction was monitored by determining the IV and OO every 15 minutes, during 3 hours. The equation of the reaction rate can be represented as shown in the Eqs. (3) to (5).

$$-\frac{d[Ep]}{dt} = -k[(H_2O_2)_0 - (Ep)] \cdot (RCOO[\![H]\!])_0 \quad (3)$$

Separating and integrating the Eq. 4:

$$\int_0^E \frac{d[Ep]}{[(H_2O_2)-(Ep)]} = k\int_0^t (RCOOH)_0\, dt \quad (4)$$

Rearranging the Eq. 5:

$$\ln[(H_2O_2)_0 - (Ep)] = -k \cdot (RCOOH)_0 \cdot t + \ln(H_2O_2)_0 \quad (5)$$

Where Ep is equivalent to the epoxide and the subscript 0 denotes the initial concentration.

Using the Eq. 5 and the experimental data, was performed a linear fit where the slope corresponds to the value of the constant k and the linear coefficient to the logarithm of the initial hydrogen peroxide concentration. The graphical representations of this study for the epoxidation of moringa oil are shown in Figure 2.

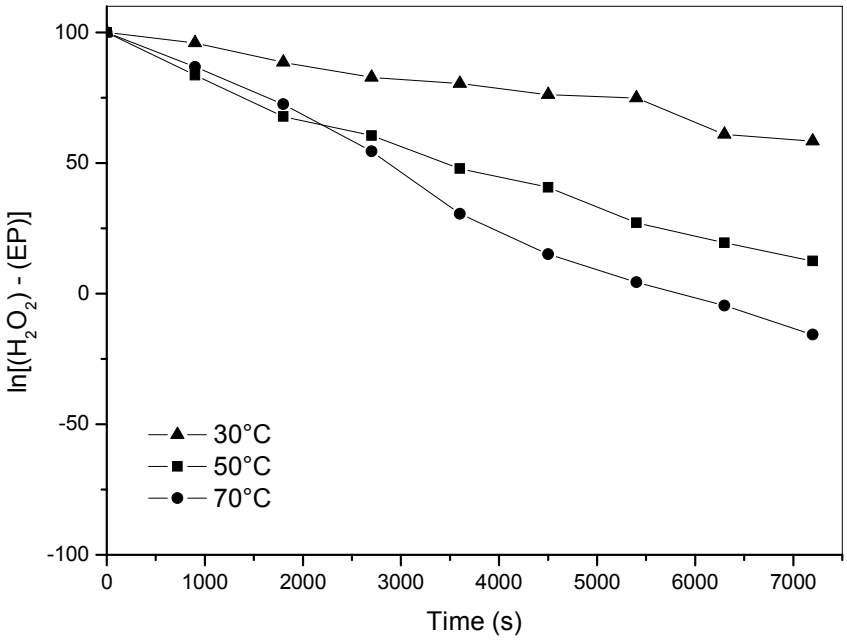

Figure 2. Graphic representation of ln[(H_2O_2) - (Ep)] versus time.

Three kinetic studies were performed at three different temperatures (30 °C, 50 °C and 70 °C) and based on the Arrhenius Equation ($k = A.e^{-Ea/RT}$) it was possible to calculate the activation energy for the reactions in study. The values of the constant k and their E_a are shown in Table 3.

Table 3. Value of the kinetic constant (k) obtained by varying the reaction temperature and their E_a.

Temperature (°C)	Rate constant of epoxidation (k x 10^{-5} L. $mol^{-1}.s^{-1}$)	E_a (kcal/mol)
30	2.11	
50	3.79	3.63
70	4.18	

These values of the activation energies are lower than those found in other studies, such as the epoxidation of mahua oil (*Madhumica indica*) in which the energy found was 14.5 kcal mol^{-1} and also, comparing to the kinetic study of epoxidation of soybean oil[7] in toluene with peracetic acid and performic acid generated *in situ*, in the presence of an ion exchange resin as a catalyst [11]. The activation energy values were 13.06 kcal mol^{-1} for the epoxidation with peracetic acid and 8.57 kcal mol^{-1} with performic acid. These differences may be justified by the fact that the epoxidation moringa oil occur faster when compared to these other studies, where the maximum values for conversion of epoxides are reached after 5 h of synthesis.

3.4. Thermodynamic Parameters.

The calculation of the thermodynamic parameters of the epoxidation moringa oil was performed from the linear fit of the Eyring Equation (Eq. 6), with the slope representing ΔH/R and the linear coefficient a relation between k_b and ΔS.

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H}{RT} + \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} \quad (6)$$

Where: k = kinetic constant;
T = absolute temperature (K);
k_b = Boltzmann constant (3.3 x 10^{-24} cal.K^{-1});
h = Planck constant (1.584 x 10^{-34} cal.s^{-1});
R = ideal gas constant (1.9872 cal.K^{-1});
ΔS = entropy of activation;
ΔH = enthalpy of activation.

Having the values of ΔH and ΔS, the Gibbs free energy (ΔG) can be calculated directly from Eq. (7):

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

In the Table 4, the values of ΔS, ΔH and ΔG for the moringa oil are presented. It is observed in the value of ΔG is greater than zero, which indicates that the reaction did not occur spontaneously.

Table 4. Thermodynamic parameters for the epoxidation reactions.

ΔH (kcal.mol^{-1})	ΔS (kcal.$mol^{-1}.K^{-1}$)	ΔG (kcal.mol^{-1})
2.93	-0.070	24.84

3.5. Conversion.

In the Table 5 are presented the values of the conversion relative to the IV for the assays of epoxidation performed in the kinetic study of the moringa oil.

Table 5. Conversion relative to the IV of the epoxide of the moringa oil.

Analysis	30 °C	50 °C	70 °C
Oxirane oxygen (%)	4.23	5.65	6.13
Iodine Value (gI_2/100g)	6.45	6.18	2.20
Conversion according to the IV* (%)	91.02	91.40	96.31

*Conversion of the IV = (IV_o - IV)/IV_o *100, IV_o = Initial Iodine Value = 71.91 gI_2/100 g

Despite the value of the conversion relative to the IV get higher at 70 °C, it is preferable to use a lower temperature (30 °C) to the synthesis of the epoxide, since that at higher temperaturesthere is a higher probability of cleavage of the oxiranic ring and the formation of undesirable secondary products.

In the Figure 3 it is noted that IV decreases with the reaction time at all temperatures. It is important to note that the better results were observed in the reduction of IV value at 30 °C compared to 50 °C. In both cases, the epoxides formed at 70 °C

reached the lowest IV. The formation of the oxiranic rings for the EPO and EMO increased with the reaction time for all evaluated temperatures, as showed in Figure 4.

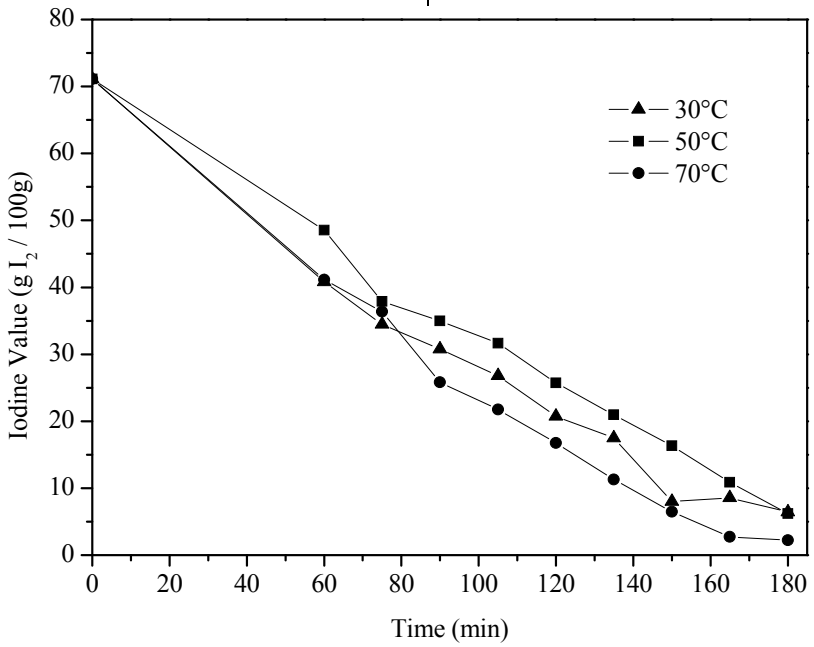

Figure 3. Graphic representation of the Iodine Value versus reaction time for the EMO at 30 °C, 50 °C and 70 °C.

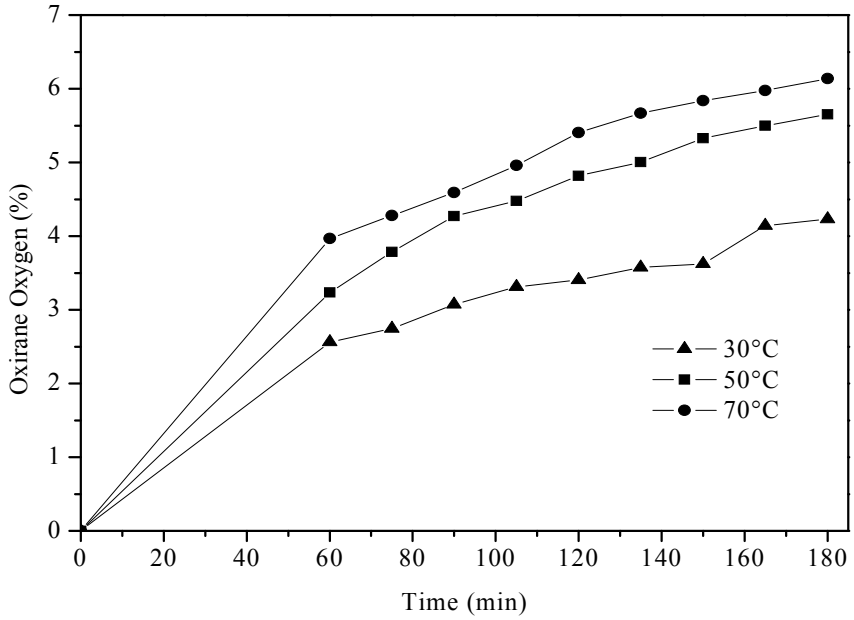

Figure 4. Graphical representation of oxirane oxygen versus reaction time for EMO at 30 °C, 50 °C and 70°C.

Analyzing the Figure 4, it is concluded that the epoxidation of moringa oil has a similar behavior in the formation of the epoxide, being directly proportional to the temperature increase. Additionally, it is noted that the behavior of the OO(%) at the temperatures of 50 °C and 70 °C are similar, being preferable to use the lower temperature (50 °C) for the epoxidation process.

3.6. Selectivity.

With the experimental values of IV and IV_0, it was possible to calculate the selectivity (S), which is a measure of non-occurrence of secondary reactions during the synthesis step. The greater the selectivity, calculated according to the Eq. (8), the lower is the occurrence of secondary reactions [11].

$$S=(EO/EO_t)/([IV_o-IV]/IV_o) \quad (8)$$

Where:

EO (%) = the experimentally determined content of epoxide oxygen per 100g of oil;

IV = iodine value of the sample;

IV_0= initial iodine value;

EO_t (%) = the theoretical oxygen content of the epoxide.

The Figure 5 shows the selectivity as a function of the reaction time for the epoxidation of moringa oil, considering the three evaluated temperatures.

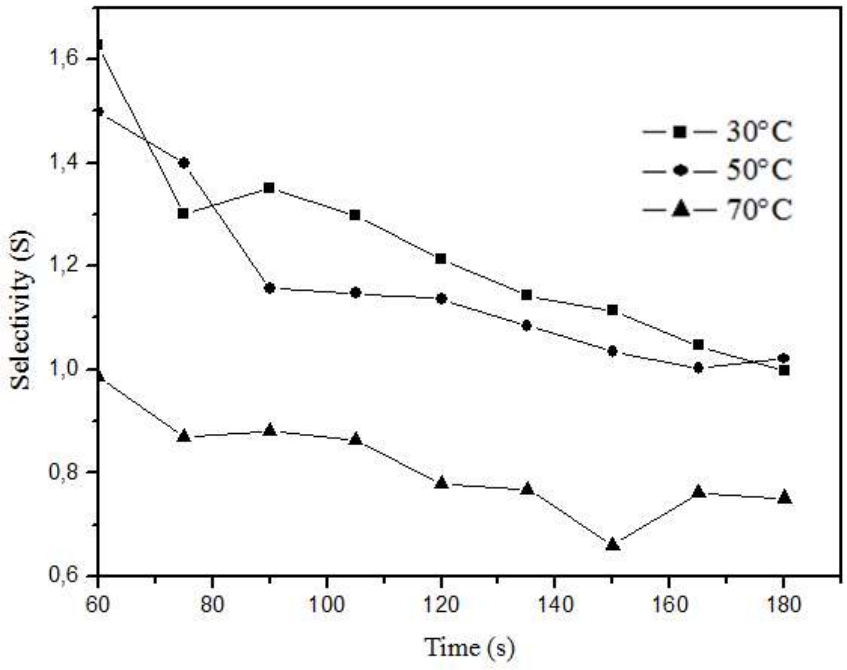

Figure 5. Graphical representation of the selectivity (S) versus the reaction time of the EMO at 30 °C, 50 °C and 70 °C.

Analyzing Figure 5 it was observed that higher values of selectivity (S) were observed at the lower temperature and, for the three evaluated temperatures, always at the beginning of the epoxidation. Moreover, it is observed that the selectivity decreases with the reaction time, a fact confirmed by Petrovic et al [11].In the synthesis at 30 °C, it is observed that selectivity values are between 1.65 and 1.10, thus indicating a low occurrence of side reactions. As the selectivity values at 50 °C and 70 °C are lower, it is recommended that the epoxidation to be carried out at 50 °C instead of 70 °C because the reaction rates are very similar. This is because the oxiranic ring cleavage in linoleic acid occurs more easily at higher temperatures [7, 13].

It is possible to affirm that a high temperature is not necessary for the formation of the EMO, because the use of 30 °C and 50 °C have obtained the most positive results of epoxy conversion with less possibility of forming other products.

4. CONCLUSIONS

This work describes an efficient approach to be applied in the oil epoxy synthesis of moringa oil. In that, the synthetic process performic acid was generated *in situ* and the epoxy conversion selectivity involves kinetic and thermodynamic analyzes, conducted by 2^{4-1} fractional factorial design with central composite resulting in a better synthetic process efficiency. The reaction was considerate as first order, the activation energy was lower (3.63 kcal/mol) and the found thermodynamic parameter was 2.93 $kcal.mol^{-1}$ for enthalpy, -0.070 $kcal.mol^{-1}.K^{-1}$ for entropy and 24.84 $kcal.mol^{-1}$ for Gibbs free energy. The applied method showed to be efficient to be applied improvement of vegetal oils epoxy synthesis. The EMO semisynthetic product could be available in the production of new raw materials.

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