

OIL EPOXIDATION APPROACH FOR PASSIFLORA EDULIS SIMS F. FLAVICARPA DEGENER

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Abstract- In this work a synthetic process applied for *Passiflora edulis Sims f. flavicarpa Degener* aiming its oil epoxy reaction in the presence of performic acid, generated in situ, was developed for its biotechnological improvement. In that, a mathematical model with four factors, two-level 2^{4-1} fractional factorial design, was employed varying temperature, reaction time, as well formic acid and hydrogen peroxide ratio. The selectivity, thermodynamic and kinetic for this epoxy reaction was also analyzed varying temperature (30°C to 70°C). In the experimental synthetic results it was observed that 2h reaction was necessary, under 50°C in the presence of $H_2O_2/C=C/HCOOH$ (1:1:1) affording $88.05\% \pm 0.5$ for the *Passiflora edulis* oil synthetic conversion and for 3h the semisynthetic epoxy derivative in the same conditions, requires 30°C ($83.09\% \pm 0.5$) avoiding oxirane ring cleavage and undesirable secondary products formation. The applied approach showed to be efficient for reactions conditions optimization in that synthetic epoxidation. The obtained semisynthetic epoxy derivative is herein described and will be replaced in the oils research progress, as a new target for chemical manufacture.

Keywords - *Passiflora edulis Sims f. flavicarpa Degener*, oil epoxy approach, performic acid, fractional factorial design.

I. INTRODUCTION

Great scientific interest has been focused on natural oil sources due its biotechnological significance. Almost 90% of the petroleum oil production is applied to transport, heat and electricity. The remaining 10% has been used as raw materials in the chemical industry for chemicals manufacture such as solvents, lubricants, synthetic plastics, rubber, detergents, paints, among other [1]. Since petroleum oil residues cause environmental problems such as contamination of waters and soils, increasing atmosphere level of carbon dioxide, biotechnological studies should be involved in the progress of oils research.

Soy, colza and sunflower oils are widely used as polymers, solvents, paints, lubricants, lubricant additives, polyvinyl chloride, polyols, glycol, synthetic plastics, rubbers, fibers, as monomers for polyamides or polyesters, detergents, among other [2].

The epoxy reaction in the presence of organic peroxyacids, which promotes the addition of an oxygen atom in the unsaturated moiety of the chemical structure of oils and fats, has been largely studied for production of semisynthetic fluids [3-6].

In order to optimize chemical characteristic of the oxiranic ring resulting from, the carboxylic acids epoxy transformation, it has been developed: oxidizing reactions process, evaluation of the reaction kinetic and

thermodynamic behavior as well as development of factorial statistical experimental design [7-18].

In the progress of the oil epoxy products it was evidenced that different sources of raw materials for new lubricants products have been widely studied. In that context, oils from jatropa, mahua, cotton, corn and sunflower, for example, have been search and applied in the chemical industry. However, some vegetable species have not been explored for oil biobased epoxy conversion, this is the case of *Passiflora edulis Sims f. flavicarpa Degener* (Passifloraceae).

The *Passiflora edulis Sims f. flavicarpa Degener* is popular known as passion fruit and its major identified compounds are unsaturated fatty acids (85%), in which 69% correspond to linoleic acid and 18% for oleic acid [19-20]. Concerning to *Passiflora edulis* native occurrence, the main Brazil producing states are Bahia, Ceará, Sergipe, Pará and Minas Gerais, corresponding nearly 80% of the available area for harvest. However, the state of Rio Grande do Norte has about 616 ha of area intended to the harvest of passion fruit, with a total production of 920.15 tons per year, being fairly representative in the remaining 20% [21].

In this present study the *Passiflora edulis* oil epoxy synthesis in the presence of performic acid, generated in situ, as a reaction medium, represent the aim of this work. The epoxy conversion process was conducted by a selectivity study conducted by 2^{4-1} fractional factorial

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design, including kinetic and thermodynamic analyzes, aiming a efficient carboxylic acids to epoxy transformation, with great amount of the semisynthetic oil epoxy product.

II. MATERIALS AND METHODS

Materials

Passiflora edulis Sims f. *flavicarpa* Degener oil was purchased in a reputable firm (Extrair Óleo Vegetal Ltda., Brazil). As preliminary results, the observed iodine value (g I₂/100g) was 130.70 and zero for oxirane oxygen (OO). Other chemicals were supplied by different company and used as received, such as: Chloro iodine sec. Wijs, formic acid (85.0%), sodium thiosulfate (99.5%), potassium iodate (99.0%) and anhydrous sodium carbonate (99.0%) all supplied by Mahal Impex Comercial Ltda. In addition, 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.

Experimental design for fractional factorial 2⁴⁻¹

In the experimental work of the epoxide synthesis applied for passion fruit oil (*Passiflora edulis* Sims f. *flavicarpa* Degener) a mathematical model was applied involving four factors, two-level 2⁴⁻¹ fractional factorial design according to a previously reported methodology [22, 23]. 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 passion fruit oil.

Factor	Unit	Level	
		Minimum	Maximum
A	H	(-) 2.0	(+) 6.0
B	°C	(-) 50.0	(+) 90.0
C	mol/mol	(-) 0.3	(+) 1.0
D	mol/mol	(-) 1.0	(+) 2.0

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.

Experimental Setup

In a 250 mL flask attached to a reflux condenser, under constant heating and agitation (500 rpm), passion fruit 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. 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.

Analytical Techniques

Iodine Value

Iodine value was determined according to Wijs method [24] 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 per 100g of sample.

Oxirane oxygen

The percentage of the oxirane oxygen was determined by direct method established by [25] using hydrobromic acid solution in glacial acetic acid. The content oxirane oxygen (OO) was calculated according to the consumed amount of the halogen atom.

Hydrogen Nuclear Magnetic Resonance (¹H NMR)

The ¹H NMR spectrum data for the oil sample and its respective semisynthetic epoxy derivative were obtained on a Bruker AVANCE® 200 NMR spectrometer, operated at 200 MHz for ¹H NMR. Deuterated chloroform was used as solvent (at room temperature) and TMS as standard. Samples were prepared at a concentration of approximately 0.25 mg/mL.

III. RESULTS AND DISCUSSIONS

The oil from *Passiflora edulis* Sims f. *flavicarpa* Degener (passion fruit) was submitted for an epoxy synthesis approach involving in the first stage vegetable oil characterization, followed by fractional factorial design 2⁴⁻¹ applied to the synthetic experimental domains as well kinetic and thermodynamic reaction investigation.

Design and optimization experiments

The Table 2 shows the values of oxirane oxygen (OO) and iodine (IV) obtained in the carboxylic acid to epoxy transformation of passion fruit oil (EPO). The fixed ratio for formic acid (0.65:1) and hydrogen peroxide (1.5:1) obeying the applied mathematical model for IV and OO, resulted in the response surfaces, as represented in Fig. 1.

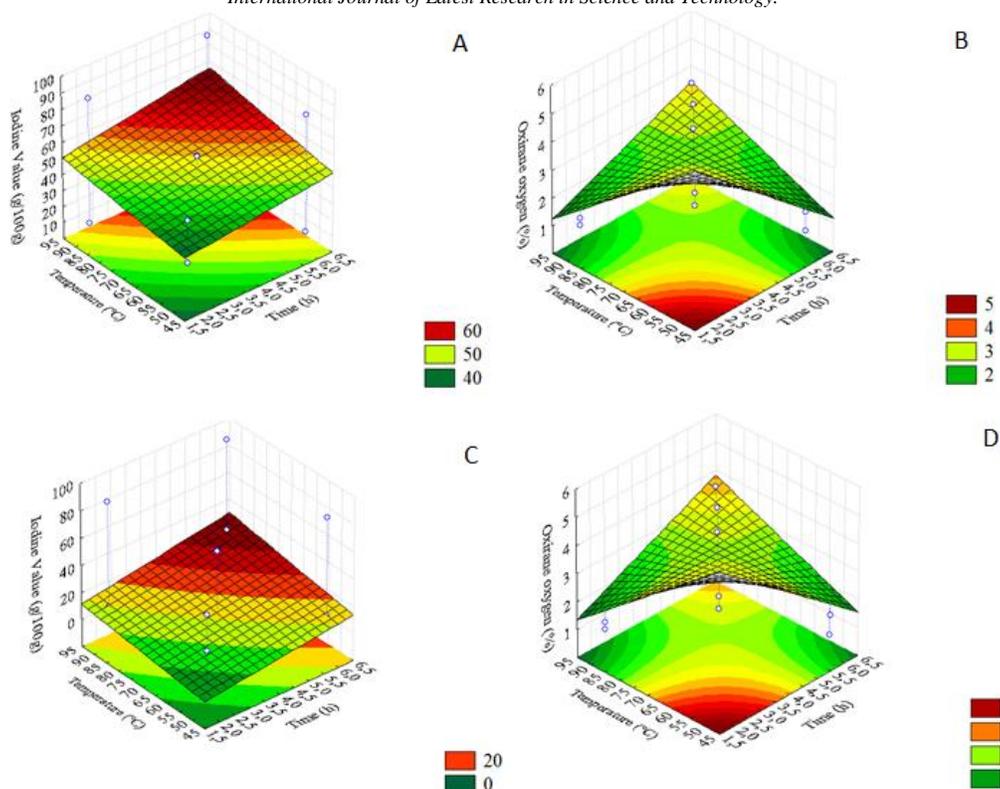


Fig.1 (A) Response surface of the EPO as a function of IV, (B) Response Surface of the EPO as a function of OO, (C) Response Surface of the EPO as a function of IV, (D) Response Surface of the EPO as a function of OO.

According to Fig. 1(A) and 1(B) the best conditions for the EPO synthesis was observed for 3 hours reaction process, under 50°C, predicting an IV around 40.00 g I₂/100 g and an OO of 5.00%; in which epoxy derivative yield does not exceed 70%. However, changes in the ratio of peroxide and acid (1:1) gives epoxide yield improvement (greater than 90%; as illustrated in Fig. 1(C) and 1(D) requiring approximately 2.0 hours of reaction at a temperature below 50°C, with iodine value smaller (without changing oxirane oxygen value).

The mathematical model applied for IV and OO values in the EPO synthetic process was obtained by linear regression, as shown in Eqs. 1 and 2, respectively.

$$Y_{IV} = 10.41 (\pm 0.12) + 13.86 [t] (\pm 0.15) + 0.20 [T] (\pm 0.15) - 61.04 [(CH_2)_2 O_2] (\pm 0.15) + 36.93 [H_2 O_2] (\pm 0.15) + 0.02 [t][T] (\pm 0.15) - 6.34 [t] [(CH_2)_2 O_2] (\pm 0.15) - 5.73 [t] [H_2 O_2] (\pm 0.15) \quad (1)$$

$$Y_{OO} = 10.03 (\pm 0.15) - 0.98 [t] (\pm 0.18) - 0.13 [T] (\pm 0.18) + 1.63 [(CH_2)_2 O_2] (\pm 0.18) + 1.08 [H_2 O_2] (\pm 0.18) + 0.03 [t][T] (\pm 0.18) - 0.56 [t] [(CH_2)_2 O_2] (\pm 0.18) - 0.50 [t] [H_2 O_2] (\pm 0.18) \quad (2)$$

TABLE 2 Oxirane oxygen (OO) and iodine (IV) values for passion fruit oil in the epoxidation reaction.

Assay	OO	IV
1	3.89	52.20
2	0.75	83.98
3	1.00	87.59
4	3.93	94.74
5	4.34	26.08

6	1.44	12.07
7	1.27	10.51
8	0.82	27.95
pc1	4.44	55.99
pc2	5.30	55.19
pc3	4.44	55.42

The optimal experimental conditions suggested by analysis of the graphs of response surfaces for EPO was verified by assay in triplicate as well as IV and OO results, which can be observed in Table 3.

TABLE 3 Characterization of the passion fruit oil and its epoxy derivative.

Analysis	Oil	Epoxy de
Iodine Value (g I ₂ / 100g)	130.7 (±0.30)	15.62 (±0.25)
Oxirane Oxygen (%)	-	5.55 (±0.20)
Conversion according to the IV	-	88.05 (±0.5)

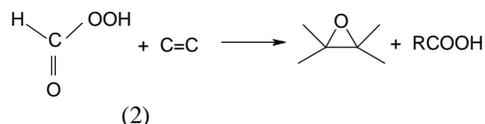
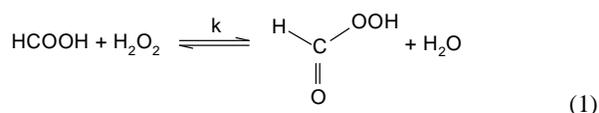
Concerning to the results presented in Table 3 the representative surface response graphic [Fig. 1(C) and 1(D)] correspond to EPO in the presence of performic acid, generated *in situ*.

Hydrogen Nuclear Magnetic Resonance (^1H NMR) Analysis

The ^1H NMR data for chemical structure of the EPO derivative compound revealed absence of the signal at approximately 5.3 ppm, corresponding to the olefin hydrogen ($\text{HC}=\text{CH}$) signal present in the target oil (which signal was observed in the target oil ^1H NMR spectrum). A signal near 2.9 ppm was associated to the hydrogens attached to the carbons epoxy cycle of the EPO derivative compound. It was also possible to confirm that the allylic hydrogens of carbons sp^2 suffered a modification shift with absorption in the region of 2 ppm to 1.6 ppm. This shift is justified by the influence of the oxygen epoxy group [26, 27].

Kinetics

The EPO reaction occurs in two steps such as reaction 01 shows the peracid formation, which act in the double bonds as an epoxidizing agent, forming the oxirane ring, as shown in the reaction 02 [9, 28].



The kinetic treatment of EPO synthesis was conducted assuming a first order reaction, in which the peracid concentration formation (*in situ*) during the reaction formation depended of H_2O_2 consumption. For the epoxy reaction great rate, the concentration of this reagent must remain constant throughout the whole synthetic process [9, 28, 29]. Thus, the reaction equation rate can be represented as shown in the equation 03.

$$-\frac{d[\text{Ep}]}{dt} = -k[(\text{H}_2\text{O}_2)_0 - (\text{Ep})] \cdot (\text{RCOO}[\text{H}])_0 \quad (03)$$

Separating and integrating this equation:

$$\int_0^E \frac{d[\text{Ep}]}{[(\text{H}_2\text{O}_2)_0 - (\text{Ep})]} = k \int_0^t (\text{RCOOH})_0 dt \quad (04)$$

Rearranging the equation 04:

$$\ln[(\text{H}_2\text{O}_2)_0 - (\text{Ep})] = -k \cdot (\text{RCOOH})_0 \cdot t + \ln(\text{H}_2\text{O}_2)_0 \quad (05)$$

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

Using the equation 05 and the experimental data results for EPO process, a linear fit was performed, in which 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 representation of this study is shown in Fig. 2.

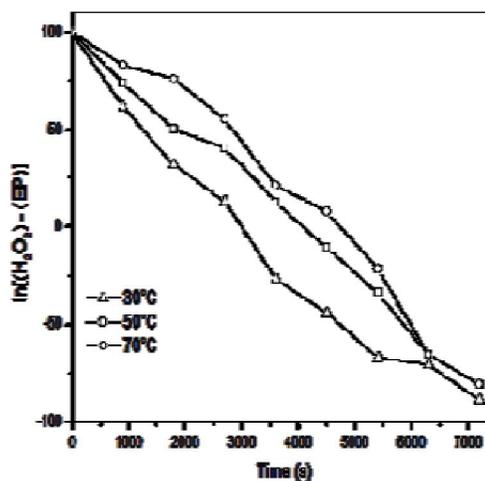


Fig. 2 Graphic representation of $\ln[(\text{H}_2\text{O}_2)_0 - (\text{Ep})]$ versus EPO time formation.

Kinetic studies were performed at three different temperatures (30°C , 50°C and 70°C). In that, the activation energy (E_a) for EPO reaction was based on the Arrhenius Equation ($k = A \cdot e^{-E_a/RT}$). The obtained values of the constant k and its E_a are shown in Table 4, in a molar ratio of $\text{H}_2\text{O}_2/\text{C}=\text{C}/\text{HCOOH}$ (1:1:1).

TABLE 4 Value of the kinetic constant (k) obtained by varying the EPO reaction temperature and its E_a .

Temperature ($^\circ\text{C}$)	Rate constant of EPO ($k \times 10^{-5} \text{ L. mol}^{-1} \cdot \text{s}^{-1}$)	E_a (kcal/mol)
30	2.50	4.36
50	4.86	
70	5.70	

The kinetic constant was $10^{-5} \text{ L. mol}^{-1} \cdot \text{s}^{-1}$, which is higher than that reported for methyl esters of palm oil and soybean oil [29, 30]. The EPO 0.90 coefficient correlation observed for all tested temperatures, allowed conclude that the cleavage of the oxirane ring can be considered negligible.

Comparatively, the obtained EPO activation energy value was lower than those found in other studies, such as the epoxidation of mahua oil (*Madhumica indica*) in which the observed energy was $14.5 \text{ kcal mol}^{-1}$ [9]. This result was equal to that observed in the kinetic study of epoxidation of soybean oil, in which the reaction medium was developed with toluene, peracetic acid and performic acid, generated *in situ*, in the presence of an ion exchange resin as a catalyst [8]. In this present study the observed activation energy values were $13.06 \text{ kcal mol}^{-1}$ for the epoxidation with peracetic acid and for performic acid, $8.57 \text{ kcal mol}^{-1}$. The E_a difference for EPO may be justified by the fact that its epoxidation occur fastest, since the maximum values for epoxy formation from these cited examples was reached after 5 h of those synthesis [8, 9].

Thermodynamic Parameters

The EPO calculation of the thermodynamic parameters was obtained from the linear fit of the Eyring equation (Eq. 06), with the slope representing $\Delta H/R$ and the linear coefficient a relation between k_b and ΔS .

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H}{RT} + \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} \quad (06)$$

in which:

k = kinetic constant;

T = absolute temperature (K);

k_b = Boltzmann constant (3.3×10^{-24} cal.K⁻¹);

h = Planck constant (1.584×10^{-34} cal.s⁻¹);

R = ideal gas constant (1.9872 cal.K⁻¹);

ΔS = entropy of activation;

ΔH = enthalpy of activation.

Since the values of ΔH and ΔS are available, the Gibbs free energy (ΔG) can be calculated directly from equation 07.

$$\Delta G = \Delta H - T\Delta S \quad (07)$$

In the Table 5, the values of ΔS , ΔH and ΔG for the EPO reaction are presented. It is observed that in both cases the value of ΔG is greater than zero, which indicates that reactions did not occur spontaneously.

TABLE 5 Thermodynamic parameters for EPO reaction.

ΔH	ΔS	ΔG
(kcal.mol ⁻¹)	(kcal.mol ⁻¹ .K ⁻¹)	(kcal.mol ⁻¹)
3.72	-0.040	16.44

Conversion for IV of EPO

Table 6 shows conversion values relative to the EPO iodine in its kinetic study. The oxirane formation data is very close for all tested temperatures. Despite of IV conversion value at 70°C, it was considered as preferable the lower temperatures, to avoid oxirane ring cleavage as well as undesirable secondary products formation.

TABLE 6 EPO iodine relative conversion analysis.

ANALYSIS	30 °C	50 °C	70 °C
Oxirane oxygen (%)	4.51	4.79	4.89
Iodine Value (gI ₂ /100g)	22.21	15.62	8.27
Conversion according to the IV * (%)	83.09	88.04	94.30

* Conversion of the IV = $(IV_o - IV) / IV_o * 100$,
IV_o = Initial Iodine Value = 130.70 gI₂/100g

It was observed that EPO has a tendency to decrease the IV value with temperature increasing (Fig. 3). However, the formation of the EPO oxirane ring increased with the reaction time for all evaluated temperatures, as showed in Fig. 4.

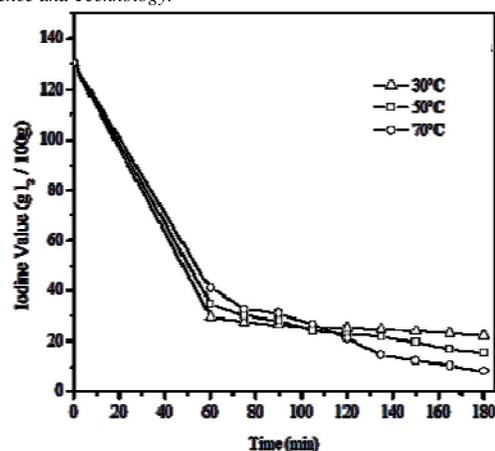


Fig.3 Graphic representation of the iodine value versus reaction time for the EPO reaction at 30°C, 50°C and 70°C.

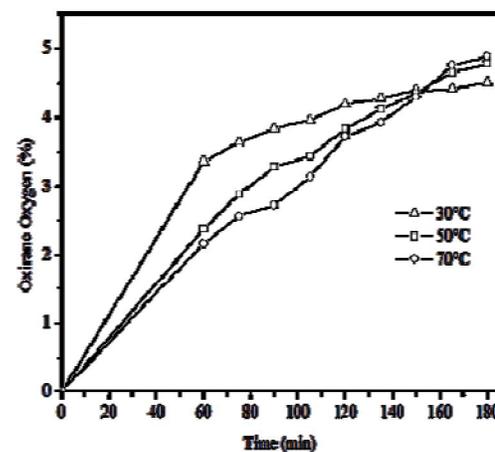


Fig. 4 Graphical representation of EPO oxirane oxygen formation versus reaction time at 30°C, 50°C and 70°C.

Analyzing the results shown in the Fig. 4 it noted that temperature influenced epoxide formation in the early reaction time, been 50°C and 70°C competitive. To avoid oxirane ring cleavage as well as undesirable secondary products formation, it was considered that the lowest temperature (30°C) is the great option for the EPO epoxidation rate.

Selectivity

Experimental values of IV and IV_o, can be used for calculate the reaction selectivity (S) value, which is a measurement for estimate the non-occurrence of secondary reactions during the synthesis steps. The search for greater selectivity was calculated according to the equation 08 [8].

$$S = (EO/EO_t) / ((IV_o - IV) / IV_o) \quad (08)$$

in which:

EO (%) = is the experimentally determined content of epoxy oxygen in 100 g of oil;

IV = iodine value of the sample;

IV_o = initial iodine value;

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

EPO reaction time considering the evaluated temperatures (30°C, 50°C and 70°C) and the selectivity parameter, it was observed that at the lowest temperature, higher S values were found (Fig. 5). In fact, EPO reaction performed at 30°C, provided selectivity values between 0.87 and 0.72, lowering the probability of side reaction occurrence. Moreover, it is evidenced that for all tested temperatures the selectivity decreases with reaction time. This results is in accordance with the soybean oil epoxidation synthesis [8] as well with the oxiranic ring cleavage in the linoleic acid epoxidation reaction which occurs more easily at higher temperatures [4, 9].

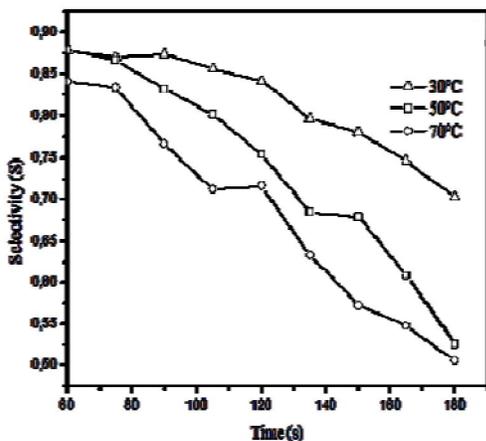


Fig. 5 Graphical representation of the selectivity (S) versus EPO reaction time (30°C, 50°C and 70°C).

IV. CONCLUSIONS

This work describes an efficient approach to be applied in the oil epoxy synthesis of passion fruit oil (*Passiflora edulis* Sims f. *flavicarpa* Degener). 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 considered as first order, the activation energy was lower (4.36 kcal/mol) and the found thermodynamic parameter was 3.72 kcal.mol⁻¹ for enthalpy, -0.040 kcal.mol⁻¹.K⁻¹ for entropy and 16.44 kcal.mol⁻¹ for Gibbs free energy. The applied method showed to be efficient to be applied improvement of vegetal oils epoxy synthesis. The EPO semisynthetic product could be available in the production of new raw materials.

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