

Thermal Degradation of β -Carotene from Macauba Palm: Mathematical Modeling and Parameter Estimation

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Abstract

Worldwide, there is a current need for new sources of vegetable oils. The natural content of total carotenoids in *Acrocomia aculeata* palm oil (up to 378 $\mu\text{g}\cdot\text{g}^{-1}$) surpasses that of many other tropical fruits, making it one of its main compositional characteristics. As far as can be verified, there is no available information on the degradation kinetics of carotenoids for *A. aculeata* oil, which is required to describe reaction rates and to predict changes that can occur during food processing. The present study considered prediction abilities that have emerged with the use of specific kinetic data and procedures to understand thermal processing better, as an essential unity operation. Two kinetic mechanisms were proposed to describe the overall thermal degradation of carotenoids in the oil; the first one consists of three reaction steps while the other presents only one-step reaction. Mass balance equations were numerically solved by a Backward Differentiation Formula technique. The kinetic parameters from both models were estimated through a hybrid optimisation method using the Particle Swarm Optimization and the Gauss-Newton method, followed by statistical analyses. The model with more than one reaction was shown to be overparameterized and was discarded. The model with a single reaction was highly suited to handle the experimental data available, and the dependency of its rate constant on temperature was expressed according to Arrhenius law. As far we know, this is the first time the kinetics of carotenoids thermal degradation in *A. aculeata* oil is investigated through modelling simulation.

Keywords: Parameter Estimation; β -Carotene; Mathematical Modeling

1 Introduction

From the perspective of extractive practices concerning oil crops, *Acrocomia aculeata*, known as macauba, is a palm tree widely dispersed in Brazil. Over the last few years, the food and chemical industries have been responsible

for most of the growing demand for vegetable oils. In this context, the interest in macauba as a food product has increased due to factors such as the nutritional quality of the oils extracted from its edible parts. The industrial interest in macauba has also involved full use of its fruit to generate co-products with added value. The fruit

mesocarp and kernel together correspond to approximately 47% (on dry basis) of the total fruit weight. Noticeably, the mesocarp contributes to around 60% (on dry basis) of the total oil content, with a predominance of oleic ω -9 (53%) and linoleic ω -6 (18%) acids. The kernel oil is predominantly saturated, with around 40% of lauric acid.

An adult *Acrocomia aculeata* palm fructifies almost throughout the year with productivity ranging from 4 to 6 tonnes of esculent oil per hectare. The crop has, accordingly, a similar productive potential to *Elaeis guineensis*, which is among the highest oil-yielding plants in the world (Evaristo et al., 2016). Considering that high yield has been an essential characteristic for the selection of commercial harvests, it has potential as an alternative oil crop that deserves further investigation (Rodríguez-Amaya, Kimura, Godoy & Amaya-Farfan, 2008). Regarding the oil extracted from the fruit mesocarp, it contains no antinutritional factors and contains up to 378 mg.kg⁻¹ of total carotenoids, mainly β -Carotene (Nunes, Favaro, Galvani & Miranda, 2015).

The carotenoids are essential pigments in fruits, these tetraterpenes (C40) synthesised by plants are secondary metabolites, necessary for photosynthesis and to prevent photo-oxidation induced by light intensities. These functions are a consequence of the light-absorbing properties of their polyene chromophore (Oloo, Shitandi, Mahungu, Malinga & Ogata, 2014; Rodríguez-Amaya, Rodríguez & Amaya-Farfan, 2006; Schieber & Carle, 2005). In general, carotenoids naturally exist as all-trans form. However, isomerisation of all-trans-carotenoids to cis forms is one of the major reactions of the compound's degradations. The critical step for losses of the component in vegetable oils remains related to the exposure to high temperature, light or pro-oxidant molecules. Indeed, the elevation of temperature during thermal treatments has been shown to dramatically increase corresponding degradation reactions rates (Achir, Randrianatoandro, Bohuon, Laffargue & Avallone, 2010; Sampaio et al., 2013).

The intensity of the thermal treatment is a critical factor that has to be controlled to increase carotenoid retention in the macauba mesocarp oil. As an essential unit operation, the thermal

processing influences both carotenoids bioaccessibility and the health-related attributes of vegetable oils (Nunes et al., 2015; Palmero et al., 2013; Rodríguez-Amaya et al., 2006).

Along with carotenoids products' identification, kinetic data become necessary to predict carotene loss on thermal degradation accurately. Kinetic evaluation is therefore required to derive necessary kinetic information for a system to describe the reaction rate as a function of experimental variables also predicting changes in a particular food system during processing. In general, most of the studies in real food report a first-order reaction on the concentration of *trans*- β -carotene, in different systems, at different processing temperatures. Although zero-order equations have also been verified, the use of a first-order kinetic is realistic in most cases. As far as we have knowledge there is no available information about thermal degradation kinetic modelling of neither β -carotene nor any other carotenoids from macauba oil (Achir, Penicaud, Avallone & Bohuon, 2011; Ahmed, Shivhare & Sandhu, 2002; Knockaert et al., 2012; Penicaud, Achir, Dhuique-Mayer, Dornier & Bohuon, 2011).

Some studies in nonpolar solvents tested reaction orders superior to one for *trans*- β -carotene degradation and found a better fit of experimental data by linearisation or nonlinear regression methods. The superior orders may be explained by the competition with isomerisation reactions, which are also of importance in vegetable oils. Most of the kinetic models used to describe *trans*- β -carotene degradation are single response kinetic models. However, as the compound is supposed to generate various degradation products, the original reaction scheme can be complex to involve complex dynamics (Achir et al., 2010; Penicaud et al., 2011; Sampaio et al., 2013). Regarding the estimation of kinetic parameters for *trans*- β -carotene degradation, the rate constants k (s⁻¹) can vary ranging from 0.00018 (120 °C) to 0.0015 (180 °C). The apparent activation energy E_a (kJ.mol⁻¹) tends to range from 80 to 110 (Achir et al., 2010; Dhuique-Mayer et al., 2007; Henry, Catignani & Schwartz, 1998; Sampaio et al., 2013).

The objective of the present study was to predict the thermal degradation of all-*trans*- β -carotene in *Acrocomia aculeata* oil through mathemat-

ical modelling, emphasizing the importance of numerical predictions for practical applications. This study is an important step to comprehend better the kinetics of thermal degradation of macauba oil, which is a promising source of high-quality raw materials.

2 Materials and Methods

2.1 Crude Oil: *Acrocomia aculeata*

Acrocomia aculeata fruit was collected from native palms with a maximum of five days after the fall in the Federal University of Minas Gerais - UFMG, located in the metropolitan region of Belo Horizonte, Minas Gerais, Brazil. The mesocarp and kernel portions were promptly separated from the fruit. Before the oil extraction, the mesocarp and kernel portions were thawed, air-dried at 60 °C for 48 hours and comminuted in an electric grinder coupled to a stainless steel cup (Goula, 2013; Pimenta, 2010). For the present study, the samples consisted of edible oil mechanically obtained from the macauba mesocarp by a continuously operated Expeller[®] press, at 34 °C. Amber glass vials (15 mL) were filled to the maximum working volume with the samples, minimising the impact of light and oxygen intrusion by reducing the volume of headspace. Samples were stored at freezing temperature (18 °C) until the analysis to minimise possible rates and extents of enzymatic lipolysis, also concerning potential losses of antioxidants (Koidis & Boskou, 2015; Parducci & Fennema, 1978).

2.2 Carotenoid Determination

The HPLC analyses of carotenoids were carried out on a Shimadzu system (Shimadzu, Japan) equipped with a vacuum degasser, a quaternary pump and an autosampler (SIL-20A HT). A UV-Visible photodiode array detector (SPD-M20A) was set in the range of 190 – 800 nm to analyse the chromatograms. Once β -carotene represent around 90% of the total carotenoids content in the *A. aculeata* mesocarp oil (Coimbra & Jorge, 2012; Nunes et al., 2015), peaks were detected

at 455 nm, and the results were expressed as all-*trans*- β -carotene. The separation was achieved at 30 °C using a normal phase column (Phenomenex Luna Silica (2) 100A Si: 250 mm \times 4.6 mm i.d., 5 μ m particle size) prior equilibrated with a flow of 0.1 mL.min⁻¹. The mobile phase was n-hexane/isopropyl alcohol (97.0:3.0 v/v), the flow rate was maintained at 1.0 mL.min⁻¹, and the elution remained isocratic until 26 min. After every 10 injections of 20 μ L, the column was reactivated with a solution of 10% isopropyl alcohol in n-hexane (v/v). The carotenoids were identified for each experimental condition by the combined use of their relative retention times and previously published UV/Vis spectra (Panfili, Fratianni & Irano, 2004; Rodriguez-Amaya, Kimura et al., 2004). The concentrations (mg.kg⁻¹) of carotenoids were expressed based on external matrix calibration (Sigma: St. Luis, MO). The spectrophotometric determination of total carotenoids (SD-TC) was performed using a Hach DR 2800 spectrophotometer (Hach, Loveland, CO, USA) as recommended by Rodriguez-Amaya, Kimura et al. (2004). The quantification (mg.kg⁻¹) considered an absorption coefficient $A_{1\%}^{1\text{cm}}$ of 2580 in high purity n-hexane (Zscheile, White, Beadle & Roach, 1942).

2.3 Thermal Degradation of all-*trans*- β -Carotene

For all the experiments, the initial carotenoid concentration (determined according to item 2.2) was applied. 0.20 mL of oil (ρ -macauba oil = 925.6 g L⁻¹) was used. The thermal treatment that supported the Model Development and the Numerical Approach was carried out in triplicate, on a dry thermo-block (SAE 1020 steel Dry-Block - CE-350; Cienlab). Aliquots of oil (2000 μ L) were placed into glass vials and inserted into the reactor. The aliquots were then heated until reaching the set temperature (t_0). Thus, the heat treatments were assumed isothermal. The temperature monitoring (accuracy of ± 1 °C) was performed based on digital thermometer probes placed into three control vials, also containing 2000 μ L of oil. The whole device was covered with aluminium foil to prevent carotenoid degradation by light. The thermal degradation kin-

etics was carried out employing at least five time sampling points, at five temperatures: For 100 °C, the experiment was run until 1500 min was reached; for 110 °C, 1440 min; for 130 °C, 270 min; for 140 °C, 160 min and, finally, for 150 °C, the experiment was conducted during 120 min.

2.4 Model Development and Numerical Approach

A first-order kinetic mechanism (Mechanism I) with three irreversible reaction steps, represented in Equations (1) to (3), was initially chosen to be tested if it can represent well the thermal degradation of β -carotene in macauba oil.



In the above equations, A represents the all-*trans*- β -carotene, B represents the oxidation and cleavage products (OCP), C represents *cis*-carotenoids (mainly, 9 or 13 -*cis*- β -carotene). Also, k_{AB} and k_{CB} correspond to the rate constants for the thermal degradation of all-*trans* and *cis*- β -carotene, respectively. k_{AC} corresponds to the carotene rate constant for the isomerisation of *trans*- β -carotene.

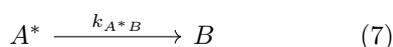
Assuming an isothermal, the material balances for all species involved in Mechanism I are represented by:

$$\frac{d[A]}{dt} = -k_{AB}[A] - k_{AC}[A] \quad (4)$$

$$\frac{d[B]}{dt} = k_{AB}[A] + k_{CB}[C] \quad (5)$$

$$\frac{d[C]}{dt} = k_{AC}[A] - k_{CB}[C] \quad (6)$$

A second mechanism (Mechanism II) was also considered to be a candidate mechanism able to predict well the experimental data available from the thermal degradation of β -carotene. This second mechanism is a simplified version of the first one, and it is shown in Equation (7).



In the above equation, A^* represents the sum of all-*trans* and *cis*- β -carotene, and k_{A^*B} correspond to the rate constant for the thermal degradation of β -carotene.

Once more, assuming an isothermal, the material balances for all species involved in Mechanism II are represented by:

$$\frac{d[A^*]}{dt} = -k_{A^*B}[A^*] \quad (8)$$

$$\frac{d[B]}{dt} = k_{A^*B}[A^*] \quad (9)$$

The ordinary differential equations resultant from the material balances (Equations (4) to (6) and (8) and (9)) were then solved using the BDF (backward differentiation formula) technique, as programmed in the DASSL code (Petzold, 1982). Parameter estimation was performed with the package ESTIMA, implemented in Fortran, using a hybrid optimisation method PSO (particle swarm optimisation) and Gauss-Newton algorithms (Brandao, Oechsler, Gomes, Souza & Pinto, 2018; Schwaab, Biscaia, Monteiro & Pinto, 2008). Five hundred particles were used, and two thousand iterations were performed with a numerical tolerance of 0.0001 for the objective function. Besides, a confidence level of 95% was considered, and all the parameters from Mechanisms I and II were estimated in their absolute form. The known weighted least-squares function was used as the objective function in the present research, and it was defined as follows:

$$F_{obj} = (y^e - y^m(x^m, \theta))^T V_y^{-1} (y^e - y^m(x^m, \theta)) \quad (10)$$

In the above equation, y^e and y^m are the vectors for the measured and predicted dependent variables, respectively; V_y is the covariance matrix of the measured outputs (assumed to be diagonal); and x^m and v are the vectors of the measured independent variables and model parameters, respectively.

Experimental variances were obtained through replicates and are illustrated in the following sections. The experimental data used to estimate the parameters was the amounts of all-*trans*- β -carotene concentration presented at certain times (A) divided by the initial amount of the caroten-

oid (A_o). Figure 1 shows the parameters estimation procedure performed in this study.

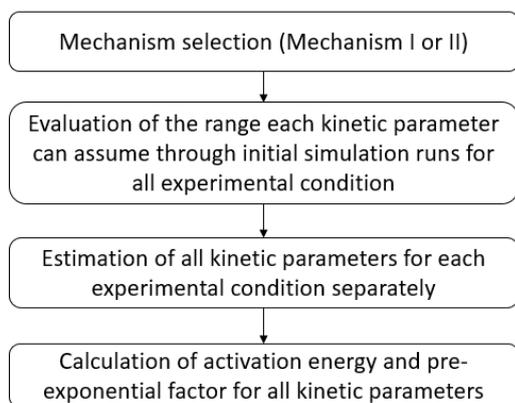


Figure 1: Flowchart of the parameter's estimation procedure

3 Results and Discussion

3.1 The task and project brief

The initial concentration of carotenoids was determined as 224.1 mg for each Kg of macauba oil. Regarding the estimation procedure, it was conducted for each experimental condition separately, as shown in Figure 1. Table 1 shows the results for the objective function, the estimated parameter and respective uncertainty obtained when model derived from Mechanism I was considered. The experimental data and the model predictions within their uncertainties are shown in Figure 2.

From Table 1, except for reaction temperatures of 140 and 150 °C, it is possible to observe that parameters uncertainties could not be calculated. Although all objective functions values were between the lower and upper limits of the χ^2 -distribution, the first model was not able to fit the experimental data available well since the model is over parametrised. At experimental conditions 140 and 150 °C, practically all parameters can assume zero value, which shows they are not significative and, consequently, they can

receive any value that won't change model prediction including zero or even negative values. Figure 2 shows that predicted and experimental profiles for the ratio A/A_0 during the reaction are in good agreement which was expected since the model has more parameters it requires, so more than one parameter combination can provide apparent good results. Since the parameters uncertainties for experiments at temperatures 100, 110 and 130 °C could not be obtained through the parameter estimation procedure, as was done for the experiments done at 140 and 150 °C, at least the parameters confidence regions for these three experimental conditions could be determined, providing an idea about the values the parameters k_{AB} , k_{AC} and k_{CB} can assume. So, Figure 3 shows the parameters confidence regions for experiments conducted at 100, 110 and 130 °C using the model derived from Mechanism I. In all confidence regions the estimated parameter values, presented in Table 1, are highlighted.

From Figure 3, it is possible to observe that, in all confidence regions, at least one kinetic parameter can assume zero value or even negative values. The regions are not well defined since parameter uncertainties are significantly high, also suggesting that the confidence region of parameters uncertainties become open (Schwaab et al., 2008), indicating estimability problems. The estimation of all parameter uncertainties simultaneously is unfeasible for these experimental conditions using Mechanism I. Based on what was said, the model derived from Mechanism I can be unconsidered as a candidate model to represent the experimental data available of thermal degradation of macauba oil.

The final objective function values for the five estimations done were between the lower and upper limits of the χ^2 -distribution. Therefore, according to the χ^2 statistical test, the proposed model fitted experimental data well, and was suitable to predict the experimental data available. Besides, all parameters uncertainties could be calculated, and they are smaller than the estimated parameters. Figures 4 shows that simulated and experimental trajectories for A/A_0 during the reaction are in very good agreement for runs conducted at 100, 110, 130, 140 and 150 °C. The model predictions adequately fitted the experimental data measured during reactions, respect-

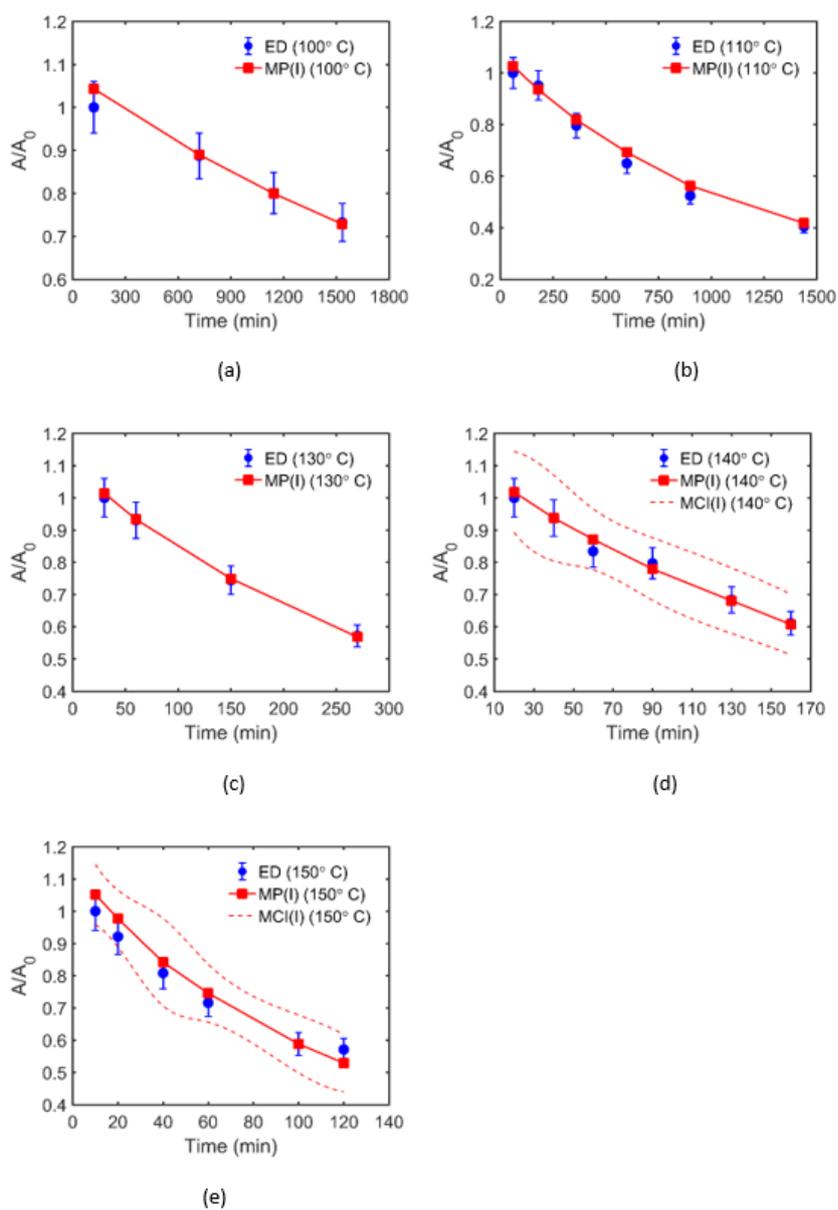


Figure 2: Predicted and experimental data at (a) 100, (b) 110, (c) 130, (d) 140 and (e) 150 °C using model derived from Mechanism I (MCI (I) = model confidence interval using Mechanism I; MP (I) = model predictions using Mechanism I; ED = experimental data).

Table 1: Parameter estimation results using Mechanism I^a

T (°C)	k_{AB} (min ⁻¹)	k_{AC} (min ⁻¹)	k_{CB} (min ⁻¹)	F_{OBJ}	X_{INF}^2	X_{SUP}^2
100	$6.44 \cdot 10^{-9}$	$2.80 \cdot 10^{-4}$	0.0404	0.53	0.0009	5.02
110	$2.45 \cdot 10^{-4}$	$6.04 \cdot 10^{-4}$	0.00922	0.80	0.22	9.35
130	$3.23 \cdot 10^{-4}$	0.00245	0.067	0.08	0.0009	5.02
140	$1.64 \cdot 10^{-5} \pm 0.0017$	0.0041 ± 0.0109	0.114 ± 1.08	0.79	0.22	9.35
150	$1.30 \cdot 10^{-9} \pm 0.0019$	0.0074 ± 0.0054	0.0872 ± 3.23	4.24	0.22	9.35

a. (T = temperature, F_{OBJ} = objective function, X_{INF}^2 = lower bound of chi-squared distribution, X_{SUP}^2 = upper bound of chi-squared distribution)

Table 2: Parameter estimation results using Mechanism II

T (°C)	k_{AB} (min ⁻¹)	F_{OBJ}	X_{INF}^2	X_{SUP}^2
100	$0.00025 \pm 1.4 \cdot 10^{-5}$	0.99	0.22	9.35
110	$0.00071 \pm 5.0 \cdot 10^{-5}$	9.70	0.83	12.83
130	$0.00246 \pm 4.1 \cdot 10^{-5}$	0.78	0.22	9.35
140	$0.00375 \pm 5.3 \cdot 10^{-4}$	1.87	0.83	12.83
150	$0.00681 \pm 1.2 \cdot 10^{-3}$	10.86	0.83	12.83

ing model and experimental uncertainties.

At this point, the remaining candidate model is only the model derived from Mechanism II. Table 2 presents the parameter estimation results using this model.

The temperature dependence on the reaction rate constant k_{A*B} is quantified by the activation energy E_a (KJ mol⁻¹) and is expressed by the Arrhenius equation represented in Equation (11). This effect of temperature on the kinetic constant k_{A*B} is shown in Figure 5. It can be observed that the estimated kinetic parameters follow the Arrhenius correlation very closely since the rate constants increase with the increase of reaction temperature. Linear regression, with a coefficient of determination (R^2) equals to 0.9891, was carried out to calculate the activation energy (E_a) and pre-exponential factor (A) for k_{A*B} constant shown in Table 2. The obtained fits can also be observed in Figure 5.

$$K_{A*B} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

In the presented Equation (11), T is the reaction temperature in Kelvin (K), A is the pre-exponential factor expressed in the same units as k_{A*B} and R is the universal gas constant (8.314 J mol⁻¹ K⁻¹).

For total all-*trans*- β -carotene degradation, a pre-exponential factor of $1.58 \cdot 10^8$ min⁻¹ and an activation energy of 83.8 kJ mol⁻¹ K⁻¹ were found. Knockaert et al. (2012) reported a rate constant at 110 °C of 0.10 ± 0.01 min⁻¹ and an activation energy of total β -carotene degradation for both an olive oil/carrot emulsion of 45.0 ± 8.6 kJ.mol⁻¹. On the other hand, Chen and Huang (1998) reported an activation energy equal to 39 kJ/mol for total β -carotene degradation of an all-*trans*- β -carotene standard dissolved in hexane. Depending on the carotenoid source, as well as on the processing conditions and the reaction medium, a range from 20 to 171 kJ/mol has been reported for the activation energy related to the thermal degradation of β -carotene (Achir et al., 2011; Achir et al., 2010; Penicaud et al., 2011; Sampaio et al., 2013). To the best of our knowledge, the kinetics of the thermal degradation of β -carotene in *Acrocomia aculeata* oil has not been investigated yet. Therefore, this result shows the thermal degradation kinetics for the all-*trans*- β -carotene in the oil agrees with those of previous studies carried out on other diverse sources of vegetable oils, since the activation energy estimated in the present study is indeed

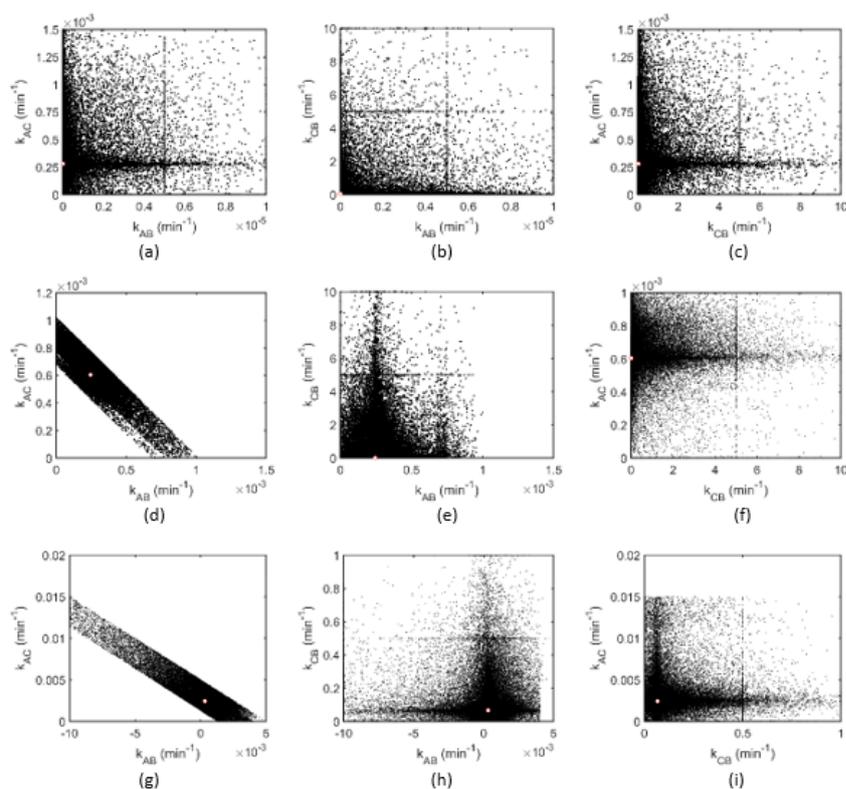


Figure 3: Parameters Confidence Regions, when Mechanism I was considered, at reaction temperature equals to (a), (b) and (c) 100 °C, (d), (e) and (f) 110 °C, (g), (h) and (i) 130 °C.

within the range reported by other authors.

4 Conclusion

The thermal degradation predicted for the of all-*trans*- β -carotene in the *Acrocomia aculeata* oil was verified through mathematical modelling. On the one hand, the use of a kinetic mechanism with more than one reaction step is unnecessary since it results in an overparameterized model. On the other hand, the model developed with just one reaction channel can simulate all the experimental conditions directly and effectively, it adequately fitted the available data within the experimental errors. The activation energy and the pre-exponential factor calculated from the Arrhenius clearly shows the dependence of the reaction rate constant k_{A*B} on temperat-

ure. The developed model with a unique reaction can be suggested to be used as an effective tool to optimise process conditions not only in laboratory but also on industrial scale. This study has provided further information enabling better comprehension of the kinetics of thermal degradation of macauba oil, which is a promising source of high-quality raw materials.

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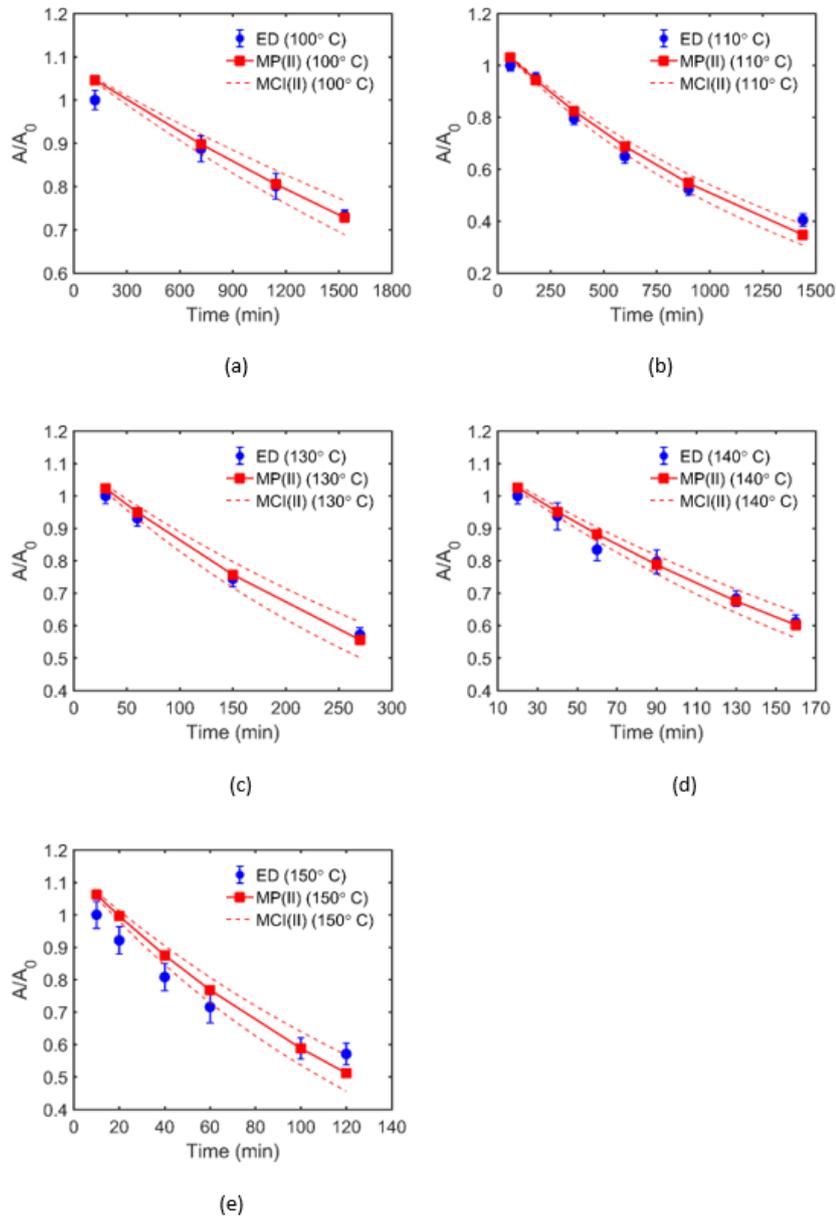


Figure 4: Predicted and experimental data at (a) 100, (b) 110, (c) 130, (d) 140 and (e) 150 °C using model derived from Mechanism II (MCI(II) = model confidence interval using Mechanism II; MP(II) = model predictions using Mechanism II; ED = experimental data).

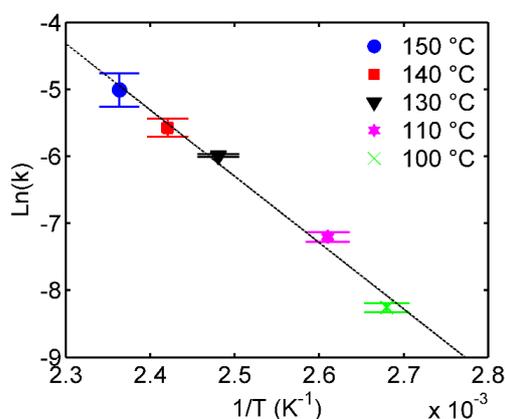


Figure 5: Arrhenius plot for the estimated model parameters at different thermal degradation temperatures using Mechanism II.

carry out this research.

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