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EDIBLE OILS MECHANICALLY EXTRACTED FROM *Acrocomia aculeata* PALM FRUIT AS NOVEL FOODS: PROCESSING, CHARACTERISATION AND THERMAL DEGRADATION KINETICS OF BIOACTIVE COMPOUNDS

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ÓLEOS COMESTÍVEIS EXTRAÍDOS MECANICAMENTE DE FRUTOS DA PALMEIRA *Acrocomia aculeata* COMO NOVOS ALIMENTOS: PROCESSAMENTO, CARACTERIZAÇÃO E CINÉTICA DE DEGRADAÇÃO TÉRMICA DE COMPOSTOS BIOATIVOS

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"The joy of Triumph could never be experienced if there were no Struggle, which is the one that determines the opportunity to Win."

Carlos Bernardo González Pecotche, Raumsol (1901-1963)

SUMMARY

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RESUMO

A presente tese de doutorado se desenvolveu a partir do objetivo geral da busca por inferências relacionadas a efeitos e condições de processamento, considerando parâmetros de qualidade de óleos vegetais mecanicamente extraídos de frutos frescos da palmeira *Acrocomia aculeata*, em estado para consumo humano, como forma de ampliar o escopo da cultura como novo alimento. Nesse sentido, de forma inédita, o trabalho investigou condições de extração mecânica e suas influências sobre a qualidade dos óleos obtidos de frutos da macaúba, para empregos polivalentes, incluindo o processamento de alimentos. Óleo virgem extraído à frio (34 °C) dos mesocarpos, o qual apresentou índice de acidez reduzido (1,6 mg $KOH.g^{-1}$), estabilidade oxidativa igual a 6,4 horas e os teores mais elevados de tocóis (85,5 $mg.kg^{-1}$), foi submetido à caracterização compreensiva em termos de qualidade, composição e identidade (índice de peróxidos, impurezas insolúveis, minerais, ácidos graxos, índices de iodo e de saponificação, viscosidade, densidade, matéria insaponificável e carotenoides totais). Os resultados foram comparados com fontes da literatura e viabilizaram a criação de uma base de referência que reforça a novidade do estudo. O potencial nutracêutico da *A. aculeata* foi destacado fortalecendo evidências científicas prévias. Modelagens cinéticas foram desenvolvidas considerando degradações térmicas de carotenoides naturalmente presentes no óleo do mesocarpo dos frutos da palmeira macaúba, visando avaliações quantitativas de efeitos de processamento. Modelo cinético de primeira ordem se mostrou apropriado para descrever a degradação oxidativa de carotenoides totais (E_a: 84 $kJ.mol^{-1}$; k_{ref}: 1,1 x 10^{-3} min^{-1}), bem como de β-caroteno e β-criptoxantina individuais (T: 373,15 K a 423,15 K). O estudo supriu a escassez de informações cinéticas relacionadas à *A. aculeata* considerando a aplicabilidade de tais dados no desenvolvimento de processos e em projetos de reatores industriais na engenharia. O potencial para utilização conjunta dos óleos do mesocarpo e da amêndoa da macauba foi apresentado, em concordância com esforços existentes no sentido da produção de *blends* vegetais, visando à melhoria de características nutricionais de lipídios estruturados com propriedades funcionais. Realizaram-se predições cinéticas como forma de avaliar efeitos térmicos sobre a retenção de carotenoids no óleo estudado (393,15 K; 120 min), contextualizando condições usuais de processo para interesterificação. A pesquisa considerou capacidades computacionais, inspirando o uso de dados e procedimentos cinéticos específicos, visando à compreensão do processamento térmico enquanto operação unitária essencial no contexto alimentício. De forma geral, a tese de doutorado avaliou efeitos e condições de processamento, integrando resultados e conhecimentos relacionados à *A. aculeata* enquanto fonte expressiva de matérias-primas para empregos multivariados, incluindo a produção de novos alimentos.

ABSTRACT

This doctoral thesis was developed with the general objective of assessing processing effects and conditions in the quality parameters of vegetable oils mechanically extracted from fresh *Acrocomia aculeata* fruit, for human consumption as a novel food. In this sense, this work has contributed with the first report on the assessment of different extractions conditions to mechanically obtain high-quality macauba oil for multi-purpose employments, including food processing. The coldly pressed (34 °C) virgin edible oil (mesocarp oil), which showed the highest tocols (tocopherol and tocotrienols) content (85.5 $mg.kg^{-1}$), the higher oil stability index (6.4 hours) and a low acid value (1.6 mg KOH g-1) was comprehensive characterized in terms of quality, composition and identity parameters (*i.e.*, peroxide value, insoluble impurities, mineral contents, fatty acids essential composition, iodine value, saponification value, kinematic viscosity, relative density, unsaponifiable matter and total carotenoids). Results were compared with literature sources to develop a baseline of information concerning the raw material, reinforcing the novelty of this study. The nutraceutical potential of *A. aculeata* was highlighted, strengthening the existing scientific evidence. Kinetic modelling involving the thermal degradation of carotenoids was performed in the macauba oil to assess food processing effects quantitatively. The results obtained between 373.15 K and 423.15 K indicated that the first order kinetic model is appropriate for describing the oxidative degradation of overall carotenoids (E_a: 84 $kJ.mol^{-1}$; k_{ref}: 1.1 x 10^{-3} min^{-1}), as well as of individual β-carotene (E_a: 80 $kJ.mol^{-1}$; k_{ref}: 1.2 x 10^{-3} min^{-1}) and β-cryptoxanthin (E_a: 87 $kJ.mol^{-1}$; k_{ref}: 1.0 x 10^{-3} min^{-1}), in the macauba oil. As kinetic data is also used in engineering design, this study filled a research gap on *A. aculeata*, gaining further insight into the reactivity of carotenoids and the macauba productive chain. The potential of jointly utilising fresh oils from macauba mesocarp and kernel was presented, for different blends of vegetable oils be attained, as a way of enhancing the nutritional characteristics of structural lipids with functional properties. Kinetic predictions were thereby carried out for making it feasible to evaluate possible thermal effects on the carotenoids retention in the oil studied (393.15 K; 120 min) which may result from interesterification processing conditions. The research timely took into account computational capabilities that have either emerged the use of specific kinetic data and procedures to understand thermal processing as an essential unity operation on food context. Overall, the doctoral thesis has assessed the processing effects and conditions, integrating results and knowledge regarding one of the highest oil-yielding plants in the world, improving the prospects of *Acrocomia aculeata* as an alternative source of high-quality raw material, for multi-purpose employments, including for producing novel food.

CHAPTER 1. Background

1.1 Introduction

From colonial times to the present day, the Brazilian economy has been characterised by recurrent cycles that also emphasise the exploitation of natural resources. In this scenario, the so-called Non-Timber Products - NTP have been shown to be capable of effectively contributing to significant changes in economic contexts. The generic term NTP is thus referred to those products obtained in forest environments, including fruits, as well as leaves and seeds, pulps and kernels, vegetable oils, among others. In addition to being able to supply local subsistences, such products also fulfil the provision of processing industries to access the growing regional and international markets (Siena et al., 2012).

In the sense of expanding and intensifying extractive practices, members of the Arecaceae family deserve to be highlighted as important sources of natural resources and raw materials for industrialisation. Particularly, the macauba palm (*Acrocomia aculeata*) has become notorious as a promising species for the production of vegetable oils in the world (Cardoso et al., 2017). With a productive potential that can reach up to 6 tonnes of oil per hectare, the crop has a similar productive potential to *Elaeis guineensis* which is among the highest oil-yielding plants in the world (Evaristo et al., 2016).

A. aculeata in effect presents several advantages related to cultivation in abiotic conditions, including its broad geographical distribution and natural adaptation to defined dry periods and different soil types. As hemerophilous species, its incorporation into agrosilvopastoral systems also contributes to the crop being one of the most widespread in the Neotropics. Especially in Brazil, native palms occur from the north to the south of the country, even though the highest concentration is found in the national Cerrado biome (Lanes et al., 2016).

Macauba crop is also distinguished by the possibility of fully utilising its fruit, in addition to the oils extracted from its mesocarps and kernels. It allows the generation of umpteen high value-added coproducts (Ciconini et al., 2013). A recent study carried out at the Universidade Federal de Minas Gerais - UFMG confirms the possibility to extract and utilise protein biomolecules obtained from substrates of mechanically pressed macauba oil. Such molecules are fundamental to human diet and animal feed and have been suggested as sources of nitrogenous biocompounds for the chemical, cosmetic and pharmaceutical industries (Grande, 2016). As a matter of fact, the vegetable and activated charcoal productions, from the fruit endocarp and exocarp, are also additional examples in the context of value addition to the crop byproducts (Rios, 2015).

It is worth noting that the scientific and economic potentials of *Acrocomia aculeata* have been highlighted by subsequent generations of researchers. Especially, studies on the palm fruit are reported to the second half of the twentieth century. Particularly, in the mid-1970s, in the wake of the petroleum world crisis, most of the Brazilian research on macauba tended to enjoy a considerable momentum promoted as a result of a Federal Government initiative which aimed to conduct studies on several oil-bearing species, for energy purposes. In the same period, Brazilian studies carried out at the Agricultural Research Company of Minas Gerais – EPAMIG stood out for bringing effective development to the cultivation of *Acrocomia aculeata.* These studies involved germination of embryos in vitro and considered the deep dormancy verified for the crop seeds to originate the first organised planting area of macauba palm trees in this same region of southeast Brazil (Arkcoll and Clement, 1989; Pires et al., 2013).

In the following decade, the Minas Gerais Technological Center Foundation had the support of the Brazilian National Ministry of Industry and Commerce to compile some of the main results obtained from the national studies conducted until that time, related to native and regional oleaginous species, among which *Acrocomia aculeata* (Rettore and Martins, 1983). In the form of a Report, such work remains contemporary among significant studies on macauba production and quality. It has also been the basis for the more recently resumption of *A. aculeata* palm research in Brazil, serving as a basis for elucidating various potentialities of the crop as an alternative raw material for applications in industrial contexts (Cardoso et al., 2017).

The end of the twentieth century and the beginning of the twenty-first, particularly, marked the continuation of Brazilian research related to the sustainable development of the macauba productive chain. Especially in 2007, technological studies were carried out for the production of pre-germinated seeds, at the Universidade Federal de Viçosa - UFV. Results from these studies enabled the potential production of large-scale seedlings, specifically in a record time of eight months. Barriers were then reduced as to the possibility of an intensification of macauba cultivation (Motoike et al., 2013, 2011). Verily, although the vast majority of *A. aculeata* stands represent natural populations on cultivated land, commercial plantations are in early stages mainly supported by private investors to be targeted at several industries (Cardoso et al., 2017).

In chronology, the assembly of a Germplasm Bank occurred from a Brazilian breeding program thus increasing both the productive possibilities and the technical perspectives for the cultivar. The development of such a program was funded by the Minas Gerais Secretariat for Science, Technology and Higher Education – SECTES, as well as being supported by the Foundation for Research Support of the Minas Gerais State – FAPEMIG. National research

groups and networks were likewise created to strengthen the context that brought together institutions, including the Universidade Federal de Minas Gerais – UFMG, the Universidade Estadual de Montes Claros – UNIMONTES and EPAMIG (Mengistu et al., 2016).

As a way to strengthen support for future studies, the Brazilian Ministry of Agriculture Livestock and Supply published the Ordinance nº 1.156 of 2008, which established a policy to identify and map the macro-regions with natural occurrences of macauba palm in the country. The referred mapping involved the identification of genotypes whose natural characteristics could be reproduced for industrial purposes (Brasil, 2008). In adherence, the state ambit Law n° 19.485 was sanctioned in 2011 by the Minas Gerais State Government. The macauba fruit cultivation, together with co-products extraction, commercialisation, consumption and transformation, was encouraged as a way of thereby sustaining *Acrocomia aculeata* along its development chain (Brasil, 2011).

Relevantly, in concomitance with the period described, continual contributions from science resulted in the awakening of macauba fruit constituents as important sources of oleaginous raw materials, with nutraceutical potential for industrial application in the food, pharmaceutical and cosmetic contexts (Hiane and Penteado, 1989; Hiane et al., 2005; Rodriguez-Amaya et al., 2008; Rufino et al. 2010; Oliveira et al., 2014; Calegari, 2015). Certainly, the mentioned contributions came to also comply with an increasing demand recently shown by consumers, concerning natural products from the food industry. Substantially, the consumption of these products tends to be associated with the health-related benefits obtained from several classes of bioactive compounds (Cataldo et al., 2016; Babbar et al., 2015; Lim and Kim, 2016).

In this ambit, it should be noted that monounsaturated fatty acids, carotenoids, tocopherols and tocotrienols, among other micronutrients, have been shown as examples of natural constituents of edible vegetable oils which are related to human blood cholesterol-lowering as well as to an inverse relationship with the incidence of coronary heart and various other human diseases. Hereupon, especially for carotenoids, these pro-vitamin A compounds, together with tocols, not only quench singlet oxygen or interact with free radicals but also contribute to vegetable oil stability due to their chemical action (antioxidant) and preservation properties (Juárez-Hernández et al., 2016; Rodriguez-Amaya et al., 2006; Lescano et al., 2015). Therefore, it is reasonable to verify that the identification of biologically active compounds, especially in oils extracted from *Acrocomia aculeata* mesocarp, indeed broadens industrial perspectives for its products (Coimbra and Jorge 2011; Ciconini et al., 2013; Nunes et al., 2015; Trentini et al., 2017).

Consistently, the first National Congress of Macauba was promoted by the Brazilian Ministry of Agriculture, Livestock and Supply - MAPA, between the years of 2013 and 2014. The Congress counted on the partnership of the Brazilian Ministry of Agrarian Development - MDA, as well as of the Brazilian Agricultural Research Corporation - EMBRAPA and the Minas Gerais State Secretariat of Agriculture, Livestock and Supply - SEAPA, to take place at the Centro Universitário de Patos de Minas - UNIPAM. The event addressed topics such as those concerning the various scientific potentials of the macauba crop while bringing together several participants from national and international research segments, as well as members of the agricultural and industrial sectors, besides authorities and academics members. The Congress programming included presentations related to relevant and contemporary scientific results and substantially included viability discussions sessions related to intensive cultivation, production practices and industrial processing of the macauba feedstock (Machado, 2016).

Given the preceding, it might be observed that in addition to overcoming short- and long-term challenges, current achievements on the presented background, together with ample prospects, tend to strengthen the basis for sustaining the macauba productive chain. It, therefore, becomes clear that the increasing socioeconomic interest in *Acrocomia aculeata* also tends to rely on continued support for research.

In this context, this doctoral thesis was developed with the general objective to assess processing effects and conditions in the quality parameters of vegetable oils mechanically extracted from fresh *Acrocomia aculeata* fruit, for human consumption, to expand its scope as a novel food. In this sense, the study is organised in chapters, also corresponding to articles, each one to define specific objectives in the proposed direction of integrating knowledge and results.

Chapter 2 reviews, bibliographically, certain topics and elements whose approaches are relevant to the progressive construction of this research work.

Chapter 3 is entitled "*A Literature Review of Thermal Degradation Kinetics: Carotenoids in Edible Macauba Oil*" and presents an article that highlights the macauba oils as alternative raw materials, with nutraceutical potential. The highly unsaturated structures of carotenoids are portrayed as responsible for the functional properties of the molecules. Such unsaturations, however, are related to processing conditions, resulting in susceptibility to thermal oxidation and isomerisation. Kinetic models are presented for describing carotenoid changes in vegetable oils. These models demonstrate relevance for process design and optimisations. The kinetics of carotenoid degradation is emphasised as being strongly dependent on the reaction medium in which these pro-vitamin A compounds are studied. In addition to the issues raised, kinetic

experiments related to *A. aculeata* oils are recommended to gain further insight into the reactivity of carotenoids and into the macauba productive chain

Chapter 4 is entitled "*Quality Parameters of Mechanically Extracted Edible Macauba Oils (Acrocomia aculeata) as alternative industrial feedstock*" and presents a comprehensive characterisation study of vegetable oils mechanically extracted from the mesocarp of fresh macauba fruit, under monitored conditions, in a state for human consumption. From approaches related to chemical and physical characteristics, as well as to quality and identity parameters, the study brings novelty when organising and discussing different data obtained in previous research on *A. aculeata* oils. Maximum levels recommended by the Codex Alimentarius are also collated thus making it possible to compare obtained data for the oil studied. The construction of a baseline for future scientific and industrial contributions is presently initiated. It is found that the collection of reference information hence brings effectiveness to access future scientific and industrial developments. Presented data are likewise in the sense of enabling the establishment of future legal standards which, to the best of our knowledge, are currently non-existent for macauba.

Chapter 5 develops the study "*Thermal degradation kinetics of carotenoids influencing macauba mesocarp (Acrocomia aculeata) oil attributes*" from kinetic modellings related to the thermal degradation of pro-vitamin A compounds naturally present in the oil mechanically extracted, at 34 °C, from the mesocarp of fresh macauba fruit. The kinetic mathematical modelling was conducted at the Dublin Institute of Technology, in Ireland. Estimates of apparent kinetic parameters, including the rate constant (k_{ref}) and activation energies (E_a), are derived from nonlinear regression. Statistical reliabilities of correlated combinations are analysed by Joint Confidence Regions (JCR, 90%) in *R* language and environment for statistical computing. The kinetic context is supplemented with thermodynamic considerations, evaluating reactions to its mechanisms, also considering enthalpy-entropy compensation as a potential phenomenon in chemical processes.

Chapter 6 is developed from the study "*Kinetic Predictions of Total Carotenoids Retention in Macauba Oil Under Interesterification Conditions*" and evaluates the simulation of possible thermal effects resulting from usually applied interesterification processes conditions on the carotenoids retention of *Acrocomia aculeata* mesocarp oil. Kinetic predictions are achieved by means of existing parameters estimated in previous studies on vegetable oils. Usual efforts to increase the nutritional and functional characteristics of structured lipids are considered. Analytical results show agreement on the distinction of fatty acids profiles between the mesocarp and kernel oils. The industrial suitability of macauba is strengthened to consider the raw materials

derived from the crop to produce blends of vegetable oils. Perspectives are added to the socioeconomic interest in *Acrocomia aculeata* as a convenient source of feedstock for multi-purpose and diverse employments.

Chapter 7 presents the *General Conclusions* in the search for integrating the knowledge and results obtained from the content of this doctoral thesis.

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CHAPTER 2. Literature Review

2.1 Vegetable oils: World supply and distribution

In recent times, significant increases have been presented for the global oilseed supply and distribution. Particularly in the bienniums 2015/16 and 2016/17 harvests, oilseed volumes of around 521 and 503 million metric tonnes were respectively produced worldwide. In the current scenario, Brazil occupies the second position in a ranking that includes the largest producers of oilseeds, only following the lead of the United States of America. Brazilian productions of oilseeds can be seen as notorious considering contributions for the 2015/16 (19%) and 2016/17 (21%) world harvests (USDA, 2017). Figure 2.1.1 makes it possible to identify other countries that stood out for such production in the biennium 2016/17.

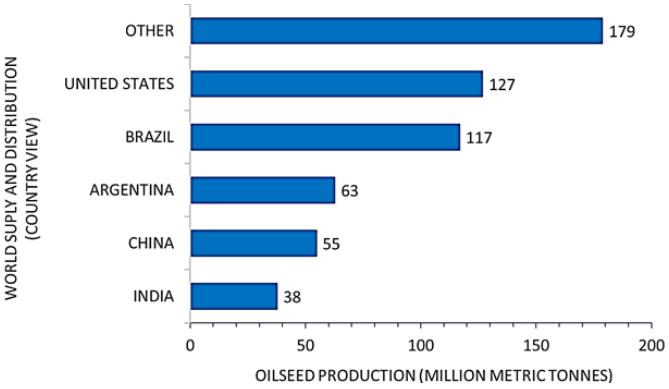

Figure 2.1.1. Major oilseeds (country view): World production (adapted from USDA, 2017).

Especially, as regards the consumption of vegetable oils obtained from oleaginous crops, continuous increments have also been emphasised (Alexandratos and Bruinsma, 2012). In the period between 2008 and 2017, the supply and distribution of this key commodity to the world economy grew by approximately 43%, reaching a production volume of 186 million metric tonnes. Importantly, projections for the 2017/18 global harvest are of sustained growth, corresponding to 195 million metric tonnes (USDA, 2013; USDA, 2016; USDA, 2017).

Figure 2.1.2 shows the world biennial progression for the supply and distribution of vegetable oils (million metric tonnes), over the last six years.

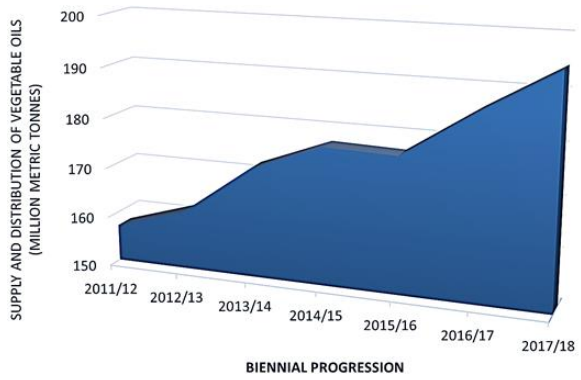

Figure 2.1.2. World supply and distribution of vegetable oils: Biennial progression (adapted from USDA, 2013; USDA, 2016; USDA, 2017).

In this context, it should be pointed out that the consumption and production of palm oil worldwide have also been following the mentioned growth trends. The production registered for this commodities came to represent 38% of the total sum that considers the volume for the further vegetable oils, in 2017. Thereupon, Figure 2.1.3 illustrates the percentage contribution of major vegetable oils in the 2016/17 world harvest, with the possibility of identifying those commodities that, besides the palm, stood out regarding production (Rival and Levang, 2014; USDA, 2017).

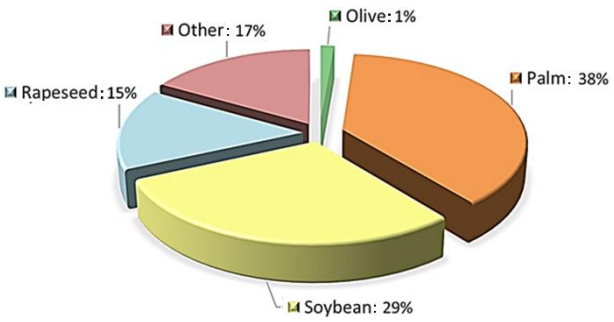

Figure 2.1.3. Major vegetable oils (commodity view): World production (adapted from USDA, 2017).

Between the years of 2012 and 2017, the Brazilian production and consumption of vegetable oils registered increases of respectively 16% and 15%. Specifically, in the biennium 2016/17, the country produced around 9 million metric tonnes of vegetable oils, contributing to values close to 5% for the global volume of vegetable oils recorded worldwide. The related domestic consumption in this same biennium (8 million metric tonnes) accounted for 4% of the 189 million metric tonnes consumed in the world, and for 90% of all the domestic production. So far, although

Brazil ranks seventh in the world ranking of vegetable oil producing countries, it is still somewhat below the productive and commercial potential, despite positive growth outlooks (OECD-FAO, 2015; Crepaldi, 2015). The major countries that stand out in the world production of vegetable oils (2016/2017 harvest) are illustrated in Figure 2.1.4.

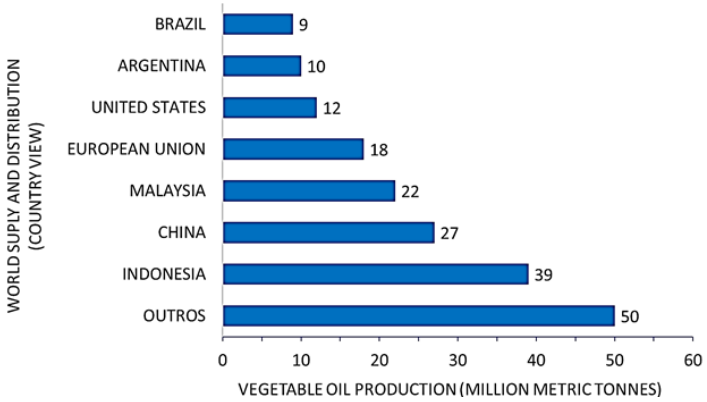

Figure 2.1.4. Major vegetable oils (country view): World production (adapted from USDA, 2017).

The growing demand for vegetable oils that is observed from the exposed scenario has been assumed to be mainly driven by food consumption and first-generation biofuels production, which also includes those derived from edible parts of food crops (Rulli et al., 2016). At this point, it becomes imperative to highlight that, besides contributing to sustaining high food prices worldwide (Figure 2.1.5), the use of edible portions of food crops for energy production comes to be one of the central ethical conflicts related to the complex interactions among food security, bioenergy and natural resource management (Kline et al., 2016).

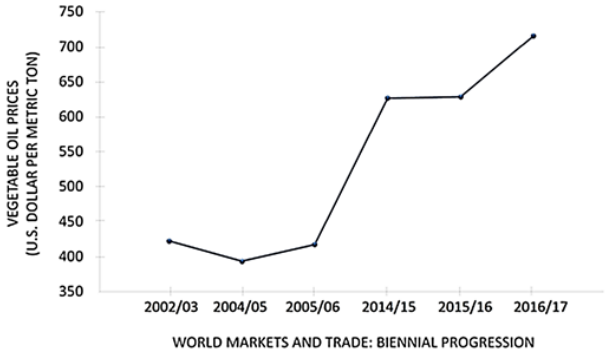

Figure 2.1.5. Vegetable oil prices worldwide (U.S. dólar per metric ton): Biennial progression (adapted from USDA, 2013; USDA, 2017).

The Food and Agriculture Organization of the United Nations states that the world population is presently in full growth to be greater than nine billion people in 2050. To duly meet this demand, it has been estimated that the need for 70% additional food will be disproportionately larger than the predicted 34% increase in population (UNDESA, 2013; Searchinger et al., 2013; FAO, 2016; Rulli et al., 2016).

For continual improvement, it is thus verified that sustainability concepts do involve assessing trade-offs among multiple dynamic goals and striving rather than achieving a specific state. Indeed, strong synergies in the current scenario require a focus on specific contextual problems and opportunities (Rival and Levang, 2014; Kline et al., 2016). There is accordingly a need for overcoming many of the issues related to food production, promoting the use of edible and non-edible vegetable oils as essential commodities for the global economy (FAO, IFAD and WFP, 2014; Plath et al., 2016).

In this sense, there is a clear need for knowledge on new sources of vegetable oils as a way to strengthen the global economy and to meet impending demands that either includes food production and consumption (Alexandratos and Bruinsma, 2012, FAO, 2016). Certainly, this context brings challenges that, distributed in short-, medium- and long term- prospects, must be overcome. Further investment in research is, therefore, still required and must rely on continuous support, also occurring from socioeconomic and governmental demands (Cardoso et al., 2017).

2.2 Macauba palm (*Acrocomia aculeata*)

2.2.1 General aspects and fruiting

Acrocomia aculeata, well known as macauba in Brazil, is an oleaginous palm tree native to tropical America. Belonging to the family Arecaceae, formerly called Palmae, macauba is one of the most widespread palms in the Neotropics. The crop occurs naturally in environments characterised by semi-deciduous forest or savanna as well as in anthropized areas such as deforested sites and pastures (Uhl and Dransfield 1987; Nunes et al., 2015; Plath et al., 2016).

Similarly to African palm (*Elaeis guineensis*), macauba (*Acrocomia aculeata*) is considered to be one of the palm tree species with the highest potential for vegetable oil production in the world (Evaristo et al., 2016; Cardoso et al., 2017). Although macauba exploitation still relies mostly on extractive activities, the crop has the advantage of being suited to edaphoclimatic zones which feature conditions averse to *Elaeis guineensis*, *i.e.*, high irradiance, low fertile soils and low water supply (Motoike et al., 2013; Conceição et al., 2012; Lanes et al., 2016).

Regarding the vegetative development, like most of the palm trees, macauba palm requires from 4 to 8 years to initiate fructification. An adult palm fructifies almost the whole year with productivity ranging from 4 to 6 tonnes of esculent oil per hectare (Nunes, 2013; Evaristo et al., 2016). Once high oil yield has been a primary criterion for commercial harvests selection, macauba notably plays an important role as an alternative oil crop, including for the food and energy markets (Rodriguez-Amaya et al., 2008; Paterson et al., 2015; Pires et al., 2013). The following Figure 2.2.1.1 shows an adult *A. aculeata* palm tree, of natural occurrence on the urban campus of the Universidade Federal de Minas Gerais - UFMG, in Belo Horizonte, Brazil.

Figure 2.2.1.1. *Acrocomia aculeata*: Macauba palm tree

Fruiting of macauba occurs throughout the year being the optimum maturation stage verified between the months of october and march (Rettore and Martins, 1983; Montoya et al., 2016). Under suitable edaphoclimatic conditions, up to 150 kg of fruit can be harvested per crop, per year. Moreover, up to 200 palm trees can be planted in one hectare of land to reach an average production of approximately 25 tonnes of fruit per hectare/year. The crop thus can respond with outputs close to 30 tonnes of fruit per hectare, to reinforce the productive potential of macauba as notorious among other tropical plants (Henderson et al., 1995; Motoike et al., 2013; Rios, 2015; Plath et al., 2016).

From a practical point of view, macauba fruit ripening is identified after its natural detachments from *Acrocomia aculeata* palm bunches which, due to its physiological development, may also indicate high oil yield and processing suitability (Caño-Andrade et al., 2006). Notwithstanding, it is worth noting that such detachment can, to some extent, lead to continuous fruit-ground contact potentiating contamination by fungi producing lipolytic enzymes. In fact, since decompositions of triglycerides are well known catalysed by lipolytic enzymes, the reactions can indeed be favoured by injury of fallen fruit and moreover accelerated by heat and light (Parducci and Fennema, 1978; Coimbra and Jorge 2012, Nunes et al., 2015).

In this sense, appropriate harvest and post-harvest procedures are to be taken into account as relevant factors when to avoid intense hydrolysis reaction of triglycerides, in turn, potentially influencing the expected yield and quality of macauba products (Cavalcanti-Oliveira et al., 2015; Evaristo et al., 2016). The following Figure 2.2.1.2 shows a set of macauba fruit attached to the bunch of a palm tree.

Figure 2.2.1.2. Set of macauba fruit attached to the bunch of a palm tree (Sikkema, 2017)

The ripe macauba fruit is spherical, slightly flattened, with diameters varying between 3.0 and 6.0 cm. The fruit epicarp (outer shell) is rigid, brittle, with a light brown colour tending to yellow. Its thickness ranges from 1 to 2 mm. As a next layer to the epicarp, the mesocarp (pulp) is yellowish, fibrous and mucilaginous. The mesocarp is readily edible, rich in glycerides and lipids, being yellowed by the presence of carotenoids. The endocarp is dark brown, hard and mainly formed by lignin and holo-cellulose. The endocarp involves the kernel (albumen) in a thin layer of integument. The kernel is yet edible and rich in lipids and proteins. Figure 2.2.1.3 shows the constituent parts of a sectioned macauba fruit (Rezende, 2009; Nunes, 2013; Ciconini et al., 2013).

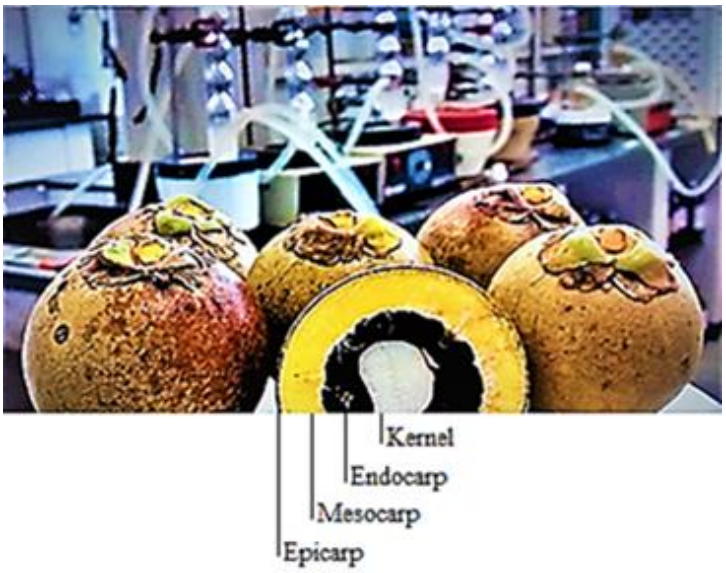

Figure 2.2.1.3. Constituent parts of a sectioned macauba fruit

The epicarp afore-mentioned contributes with around 24% (*w/w*) for the fruit total weight. The mesocarp, endocarp and kernel respond to around 40%, 29% and 7% (*w/w*) of the fruit total mass, respectively. Figure 2.2.1.4 illustrates a funnel plot concerning the relative contribution of constituent parts to the total mass of fresh macauba fruit. Although the physical and chemical characteristics of macauba fruit are widely known to vary among locations and regions, depending on seasons, genotypes and maturation stages (Rettore and Martins, 1983; Ciconini et al., 2013; Pires et al., 2013; Evaristo et al., 2016), the following composition may be taken as representative for fresh mesocarps and kernels (Cardoso et al., 2017), respectively: moisture (62%, 15%), lipids (30%, 27%), proteins (3%, 12%), carbohydrates (7%, 47%) and ash (2%, 2%).

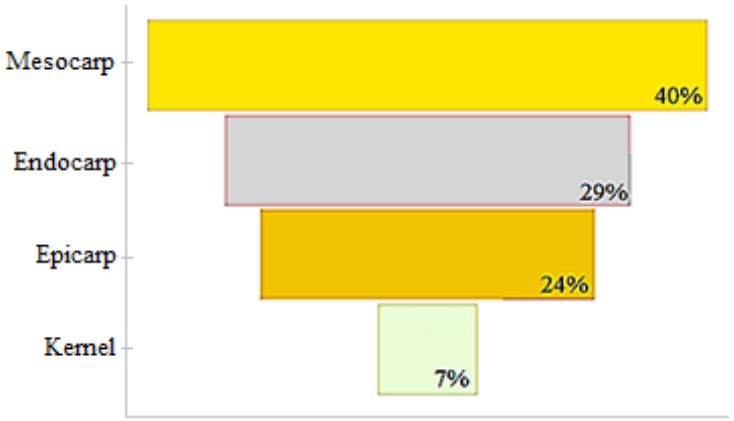

Figure 2.2.1.4. Relative contribution of each constituent part to the macauba fruit (Adapted from Silva and Andrade, 2013; Rettore and Martins, 1983)

2.2.2 Macauba mesocarp and kernel oils

From the knowledge that arises when elucidating the constituent parts of *A. aculeata* fruit, the obtainment of esculent oils has definitely to be highlighted (Pires et al., 2013; Evaristo et al., 2016). Similarly to *Elaeis guineenses*, two different types of oils can be obtained from the edible parts of macauba fruit (Hiane et al., 2005; Coimbra and Jorge, 2012; Nunes et al., 2015).

The oils obtained from the macauba mesocarp and kernel have different physical and chemical characteristics. Particularly, the crude mesocarp oil contains small amounts of solid sediments and a very characteristic odour that is typical of ripe fruit. The oil is a yellowish red colour, mainly due to the presence of carotenoids. Especially, the predominance of unsaturated fatty acids composition (up to 77%) is emphasised to be included later with the physical and chemical characteristics featured in this thesis. Regarding the oil obtained from the kernel of macauba fruit, its colour is translucent yellowish to colourless due to the presence of natural pigments, among which chlorophylls, tocopherols and also small amounts of carotenoids. Its essential composition, in turn, is predominantly of saturated fatty acids (up to 70%) (Rettore and Martins, 1983, Oliveira et al., 2014; Silva et al., 2016; Trentini et al., 2017).

Del Rio et al. (2016) and Cardoso et al. (2017), take into account the well known physical-chemical dissimilarity between the macauba mesocarp and kernel oils to emphasise the potential of these raw materials to meet industry and market demands in different ways. The authors further point out that the predominance of oleic acid as a result of saponification process of mesocarp oil (around 55%), and lauric acid from kernel oil (around 32%), consist of a significant difference between these two oils, both of which present high thermal stability, with higher stability of mesocarp oil. Figure 2.2.2.1 shows the edible oils obtained from fresh macauba fruit.

Figure 2.2.2.1 Edible oils mechanically obtained from fresh macauba fruit

In adherence to the context, once physical and chemical characteristics, tend to influence the functional properties of vegetable oils, as well as of intermediate and structured edible products, chosen terms for varied industrial applications of these raw materials may as well be dependent on natural attributes. In fact, from an economic point of view, such characteristics are usually related to processing feasibility. Thus, considering current trends in generating scientific knowledge concerning alternative sources of vegetable oils, future results thereon shall be accumulated in a directed manner and designed to answer fundamental questions, including those of industrial applications for real food systems (Kadhum and Shamma, 2015; Patel and Dewettinck, 2016).

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CHAPTER 3. A Literature Review of Thermal Degradation Kinetics: Carotenoids in Edible Macauba Oil

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Abstract

Recently, the food and chemical industries have been responsible for most of the growing global demand for vegetable oils. From the perspective of extractive practices concerning oil crops, macauba (*Acrocomia aculeata*) palm tree enjoys a wide dispersion in Brazil. The industrial interest in macauba has also involved full using its fruit to potentially generate co-products with added value, in addition to the oils extracted from its edible mesocarp and kernels. Notably, relatively high amounts of carotenoids have been found in the oils obtained from the macauba mesocarp to adhere with the growing interest of industries and consumers regarding nutraceutical food. In this sense, on the one hand, it becomes reasonable to stand out that the highly unsaturated structures of carotenoids respond for leading the compounds to functional properties. On the other hand, it creates challenges about stability, including during thermal processing. Kinetic models describing carotenoid changes are valuable tools for design and optimisations as a function of process parameters. Thus, kinetic experiments related to macauba esculent oils are recommended to gain further insight into the crop productive chain as well as into the reactivity of carotenoids.

Keywords: macauba, thermal processing, carotenoids, kinetic modelling.

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3.1 Introduction

From the perspective of extractive practices concerning oil crops, *Acrocomia aculeata*, known as macauba, is considered a palm tree with greater dispersion 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 been embraced by factors such as the nutritional quality of the oils extracted from its edible parts. 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 (Pimenta et al., 2012; Rettore and Martins, 1983).

In a hectare of Brazilian native land, up to 200 palm trees can be found representing a production close to 25 tonnes of fruit/year, which is notable among other vegetables grown in the country's soil (Caño Andrade et al., 2006). Fruiting of macauba occurs throughout the year and shows great maturity stage between the months of October and March. Briefly, in what refers to the quality parameters of macauba fruit, Farias (2010) points out that it tends to be determined by the association of various attributes, combining physiological factors (*i.e.*, the level of development and maturity) with physicochemical factors.

Especially, bringing the focus of quality to minor compounds, the crude macauba oils tend to contain around 5% of non-glyceridic materials. These materials are formed, among others, by different quantities of phospholipids, free and esterified sterols, squalenes, phenols, liposoluble vitamins, free fatty acids, oxidation products, mono and diglycerides, metals traces, chlorophyll, carotenoids, tocopherols, and other colouring compounds (O'Brien, 1998).

Particularly, carotenoids and tocopherols are components that stand out among other minor ones due to their chemical action (antioxidant) and preservation properties. The nutraceutical potential of these both components worth to be mentioned once it evidences the oils extracted from *Acrocomia aculeata* fruit as potentially beneficial foods for human health. Highlighting the oil extracted from the macauba mesocarp, its colour ranges from yellow to red being inherently attributed to the presence of carotenoids. The concentration of these pro-vitamin A compounds in the oil can be as high as 378 $mg.kg^{-1}$. Importantly, the colour for the kernel oils ranges from white to translucent yellow, due to tocols, chlorophyll and also to small amounts of carotenoids (Rodriguez-Amaya et al., 2008; Coimbra, 2010; Pimenta et al., 2012; Nunes et al., 2015).

In view of the foregoing, it is relevant to highlight that recent studies on the global food market indicate new trends and requirements for human feeding by grouping them into five categories: Healthiness and Welfare; Sustainability and Ethics; Pleasure and Sensoriality; Convenience and Practicality; Quality and Reliability. With effect, the Brazilian food industry has indicated the understanding of these new trends. Moreover, the national vegetable oil market has adherently shown signs to consider diversification and value addition as a bias for its products (Barbosa et al., 2010). It is, thus, noticeable that the oils extracted from macauba fruit may cohere with health benefits to be potentially applied as an alternative feedstock for the production of functional food with special appeals (Rettore and Martins, 1983; Prates-Valério et al., 2014; Pimenta et al., 2012).

It is, therefore, reasonable to stand out that the highly unsaturated structures of carotenoid may lead to their functional properties at the same time that it creates challenges about stability along thermal processings. The compounds are expected to undergo two changes as a result of exposure to high temperature, light, and pro-oxidant compounds: oxidation and isomerisation (Rodriguez-Amaya et al., 2008). Degradation should then be naturally prevented to maintain biological activity. Hence, quantitative kinetic models describing carotenoid changes as a function of process parameters are valuable tools for predictive processing optimisation. Carotenoids conversion kinetics is strongly dependent on the food system as well as on the compound type. Thus, accurate knowledge on thermal degradation kinetic becomes determinant to quantitatively predict specific changes that occur, also, in macauba oils (Rodriguez-Amaya et al., 2008; Sampaio et al., 2013; Colle et al., 2013).

3.2 The Review

3.2.1 Carotenoids

According to Lewinsohn et al. (2005), carotenoids are among the most important pigments in fruits. These tetraterpenoids (C40) synthesised by plants are secondary metabolites, essential 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. Carotenoids consist of two classes of molecules: carotenes (hydrocarbons); xanthophylls (contains at least one oxygen function). The β-carotene, which belongs to the first class, is the most widespread in foods. The following Figure 3.2.1.1 presents major chemical structures for some carotenoids which, together with β-carotene, present the before-mentioned relevance for human feeding and health.

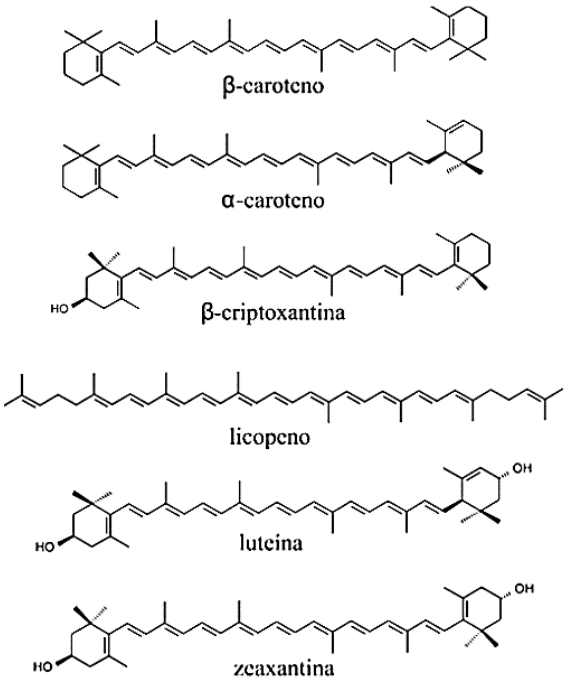

Figure 3.2.1.1. Carotenoids with relevance to human health (Rodriguez-Amaya and Kimura, 2008).

Drawing attention to β-carotene, along with α-carotene and β-cryptoxanthin, the compound is a vitamin A precursor due to its structure analogous to that of vitamin A dimers. Indeed, its structure is stoichiometrically equivalent to two molecules of retinol. Potentially providing 100% activity, β-carotene has been highlighted as an important source of vitamin A in developing countries. The compound can also act as an effective antioxidant because of its highly delocalised electrons which can stabilise intermediates such as carbocations or radicals formed by resonance reactive. This particular carotenoid can thus protect cellular tissues by quenching singlet oxygen and scavenging active free radicals that are involved in potentially lethal processes, such as lipid peroxidation (Pénicaud et al., 2010).

The highly unsaturated structure of β-carotene includes a significant number of double bonds which also makes it considerably sensitive to degradation. The β-carotene chemical formula is $C_{40}H_{56}$. It is composed of eight isoprene units (C_5) with specific end groups or two β-ionone rings. The compound is lipophilic, insoluble in water and soluble in organic solvents (*i.e.* petroleum ether, hexane). The β-carotene physical, chemical and biological properties are mainly derived from the mentioned long sequence of conjugated double bonds. Firstly, the single and double bond alternation causes the delocalisation of the π electrons and makes the absorption of light possible within the range of the visible spectrum. β-carotene absorbs blue and purple light with a maximal at 450 nm and thus has an intense red-orange colour (Rodriguez-Amaya et al., 2008).

3.2.2 Degradation reactions

In general, carotenoids naturally exist as all-*trans* form. However, as previously discussed, isomerisation of all-*trans*-carotenoids to *cis* forms is one of the major reactions of the compounds degradations. Therefore, considering that *trans*-β-carotene concentration increases during fruit ripening – including macauba – its level stagnates or tends decrease at post-harvest steps. Even so, 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 the corresponding degradation reactions rates (Dellamonica and Mcdowell, 1965; Achir et al., 2010; Sampaio et al., 2013).

The main degradation products identified after carotenoids and food processing are isomers, oxidation and cleavage products. Current thinking is that the whole process firstly involves isomerisation of all-*trans*-carotenoids to *cis*-isomer, followed by the formation of a resultant di-radical. The reactions may also occur simultaneously and reversibly. The following Figure 3.2.2.1 illustrates the chemical structures for the most common isomers involved in thermal degradations of β-carotene, in vegetable oil systems (Zechmeister, 1962; Rodriguez-Amaya et al., 2008).

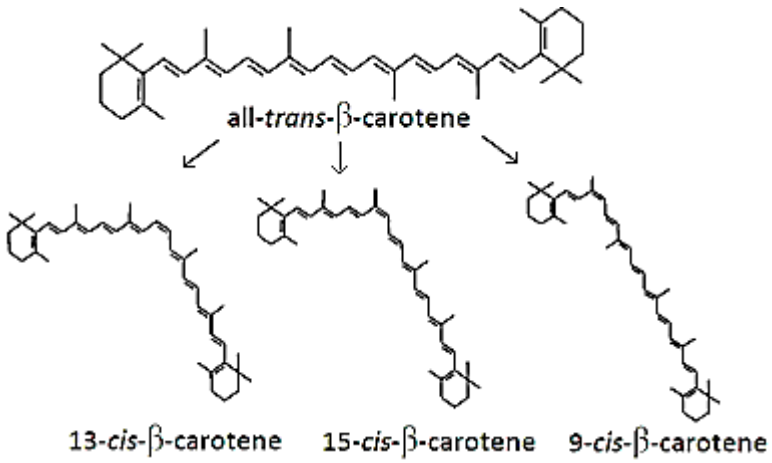

Figure 3.2.2.1. β-carotene Isomers: Thermal degradations (Rodriguez-Amaya et al., 2008).

From the beginning of heating processes 13-*cis*- and 9-*cis*-β-carotene are commonly detected. *Cis*-carotenoids isomers are reported to present residual vitamin A potential (about two-fold less when compared to *trans isomers*) besides lower colouration power and reduced antioxidant properties. It should be pointed out that, as well as *trans*-β-carotene, the isomers 13-*cis*-β-carotene and 9-*cis*-β-carotene tend to be involved in degradation reactions which infer relevance in the monitoring of their formations and degradations (Achir et al., 2010; Zechmeister, 1962).

3.2.3 Carotene determinations

Over the last few years, the scientific community has invested continuous efforts regarding the correct determination of reliable data related to the presence of carotenoids in food matrices. In what it refers to analytical procedures, the uncertainty of those that can be used interchangeably for all foods is explained in the complexity of the task itself. As discussed, the carotenoids widespread in nature present several chemical structures and diverse pro-vitamin potential. Also, concentrations are too varied to happen for different matrices (Rodriguez-Amaya et al., 2008).

Analytical methods for the determination of carotenoids in complexes matrices are purposed in numerous studies usually including advanced techniques. In particular, for food, trends in the analysis of the mentioned compounds not only reflect the advances in analytical instrumentation but do incorporate new knowledge about the role of these compounds in human health. It is well known, however, that advanced techniques are costly. Thus, many analytical procedures have been continually developed with the purpose of establishing simple, rapid and inexpensive procedures for determining carotenoids and pro-vitamins A in foodstuff (Teixeira-Godoy, 1993).

The first methods for determining these compounds in food matrices were based on open column chromatography (OCC) technique. The latest methods are based on High-Performance Liquid Chromatography (HPLC) as well as on related practical techniques, including ultra performance liquid chromatography, mass spectrometry, among others (Rodriguez-Amaya and Kimura, 2004; Colle et al., 2013). From the chemical aspect, the saponification is a procedure to be included before chromatography which has been applied to remove unwanted lipids and chlorophylls, eventually hydrolysing carotenoids esters. This operation, however, is included only when necessary once it extends the time of analysis and can promote the formation of artefacts and carotenoids degradation products (Godoy and Rodriguez-Amaya, 1993).

Because carotenoids absorb maximally at different wavelengths and have different absorption coefficients, some results obtained from normalisation (area percentages) can only be taken as approximate relative proportions. For food science and nutrition purposes, however, these results are useful if presented regarding concentration, that is, the weight of the pro-vitamin per unit weight of the sample. It can thus be done in HPLC using internal or external calibration curves, for which the concentrations of the standards may also be determined spectrophotometrically. It is emphasised that analytical methods for the determination of total carotene content may be suitable to the nature of each sample. This suitability is one of the main requirements for obtaining reliable data on carotenoids. In this context, among other minimum criteria, particularly related to spectrophotometric identifications of carotenoids, there is an imperative need to correctly set

the absorption spectrum in the adequate UV-VIS region of the determined compound (Rodriguez-Amaya and Kimura, 2004; Rodriguez-Amaya, 1997; Davies; 1976).

The vitamin A value of food can be determined based on what is called "β-carotene fraction" or "total carotene". The method is recommended by the AOAC (Deutsch, 1990). Nevertheless, the mentioned method is appropriate only when β-carotene is both the most widely distributed carotenoid and the most active pro-vitamin A in the analysed food and coproducts, as particularly occurs for macauba oils. For food in which the fraction of β-carotene becomes smaller compared to that of other active carotenoids, the result can be overestimated. In turn, if active carotenoids are not included in this fraction, the result can be underestimated, *i.e.*, papaya, cashew and pumpkin (Rodriguez-Amaya, 1989; Godoy and Rodriguez-Amaya, 1993).

3.2.4 Degradation kinetics

Along with carotenoids products identification, kinetic data become necessary to predict carotene loss on thermal degradation accurately. In this sense, kinetic evaluation is 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 (Zao, 2011; Dong-Sun and Hyun-Ku, 1989; Henry et al., 1998; Ahmed et al., 2002) 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 (Pénicaud et al., 2010).

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. The majority 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 is complex and of high dynamics (Pénicaud et al. 2010; Sampaio et al., 2013; Achir et al., 2010; Crandall et al., 1983). 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 (Dhuique-Mayer et al., 1997; Henry et al., 1998; Sampaio et al., 2013; Achir et al., 2010; Crandall et al., 1983). With relevance, the rate constants (k) are assumed to vary according to the Arrhenius law as the temperature dependence is often given by the related equation 1.

$$k = k_0 \, exp^{\left(\frac{-E_a}{RT}\right)} \quad (1)$$

Where,

k = Specific Rate Constant

k_0 = Pre-Exponential Factor

E_a = Activation Energy (J.mol^{-1})

R = Gas Constant (8.314 J.mol^{-1} K^{-1})

T = Absolute Temperature (K)

Predominantly, experimental data are presented in functions of *C* and C_0 at different heating time intervals *t*, where *C* is the carotenoid concentration (mg.kg^{-1} of oil) at each time *t* and C_0 is the amount of carotenoid when the trial reaches the desired temperature (isothermal temperature). The following general differential equation (2) is widely applied for carotenoid changes in complex systems (Sampaio et al., 2013).

$$\frac{dC}{dt} = -kC^n \quad (2)$$

The presented equation (2) conveys that the degradation rate *dC/dt* is proportional to the nth power of carotenoids concentration (*C* in mg.kg^{-1} of oil) at any time *t*, while *n* is the order of the reaction and *k* (1/time) is the reaction constant (Sampaio et al., 2013).

It should be noted that, in a research carried on by Achir et al. (2010), the kinetic approach of *trans*-β-carotene is presented for enriched vegetable oil systems. The study presents different thermal sensitivities depending on the carotenoids type also stating the influence of the initial oil quality and composition on the carotenoid degradation. The authors affirm that low peroxide value and high tocol content can limit carotenoid oxidation. In conclusion, it is recommended to work at low temperature for a long time instead of a high-temperature-short-time treatment.

Zepka et al. (2009) proposed a multi-response model to represent carotenoid degradation in cashew apple juice. Considering simultaneous apparition and disappearance of intermediary products, the mechanism involves parallel irreversible and reversible reactions of *trans*-β-carotene to yield mono-*cis*-isomers. Therefore, as a result of the products global monitoring, the authors determined different constant rates, discriminating two pathways and similarly evaluating the effect of temperature supply on carotenoid degradation.

Colle et al. (2013) compare the thermal degradation and isomerisation of β-carotene and lycopene in the presence of lipids. A single response modelling approach was used to study the degradation reaction, while multi-response modelling was applied to describe isomerisation reactions and products: 13-*cis*-β-carotene, 9-*cis*-β-carotene and 15-*cis*-β-carotene. In conclusion, the results show that carotenoids conversion kinetics are strongly dependent on the carotenoid type as well as on the food system they are contained. It is affirmed that process optimisation does demand specific kinetic data.

3.3 Final considerations

Over the last decades, the vitamin A deficiency has been recognised as a major public health problem in developing countries. In this context, the interest in macauba (*Acrocomia aculeata*) as a food product is also embraced by the nutritional quality of its edible oils. Carotenoids give to the crude macauba mesocarp oil the distinctive orange-red colour. Therefore, together with tocopherols, the mentioned tetraterpenoids contribute to the stability and nutraceutical value of the esculent oil. Consumers and industries have recently shown a growing interest in exploring the potential of several functional raw materials. Given the preceding, it shall be noted that the nutritional quality of the macauba oils may be dependent on the processing steps to which such alternative feedstock might be subjected depending on the ample possibility of application. In this scenery, isomerisation and oxidation must be pointed out as the most significant reactions of carotenoids degradation that may occur during thermal processings involving the compounds. Thus, kinetic models describing carotenoid quantitative changes as a function of process parameters are valuable tools for vegetable oil processing optimisations. Kinetic models used to describe carotenoids degradation are usually single response. In general, most of the studies about *trans*-β-carotene degradation in oil systems report a kinetic behaviour outlined by first-order reactions. Nevertheless, superior reaction orders may explain possible competitions occurring between isomerisation-oxidation reactions of carotenoids degradations. Carotenes degradations are highly dependent on many factors linked to the medium in which they are contained. Such a finding could be one of the reasons why only a few kinetic parameters are currently available in the literature. Furthermore, several studies mainly deal with β-carotene degradation. In addition to the issues raised, considering a research gap on kinetic data related to *Acrocomia aculeata*, kinetic experiments concerning its edible oils become strongly recommended to gain further insight into the reactivity of carotenoids and more importantly into the macauba productive chain.

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CHAPTER 4. Quality Parameters of Mechanically Extracted Edible Macauba Oils (*Acrocomia aculeata*) as alternative industrial feedstock

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Abstract

There is a current need for knowledge on new sources of vegetable oils. Macauba palm (*Acrocomia aculeata*) has been regarded as a promising alternative source to meet food and industrial demands. With a similar productive potential to African palm (*Elaeis guineensis*), this crop is among the highest oil-yielding plants in the world. The present study has characterised the macauba mesocarp oil comprehensively with the objective to aid the setting up of standards encompassing the quality, composition and identity. Samples were obtained under five different pressing conditions and screened regarding quality parameters. The coldly pressed sample (M1), which showed the highest tocols (tocopherol and tocotrienols) content (85.5 $mg.kg^{-1}$), the higher oil stability index (6.4 hours) and a low acid value (1.6 mg $KOH.g^{-1}$) was characterised in terms of chemical, physical and identity characteristics, *i.e.*, peroxide value, insoluble impurities, mineral contents, fatty acids essential composition, iodine value, saponification value, kinematic viscosity, relative density, unsaponifiable matter and total carotenoids. Results were compared with literature sources to assess *A. aculeata* as an alternative feedstock. The present study contributes to the evidence that products derived from macauba may have good consumer acceptance, a potential nutraceutical value and natural appeal. It is suggested that the compliance to legal standards must be continuously pursued to guarantee the sustainability of the productive crop chain.

Keywords: edible oils, macauba (*Acrocomia aculeata*), chemical and physical characterisation

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4.1 Introduction

The world consumption of vegetable oils has increased significantly in recent years. Between 2008 and 2017, the use of this key commodity grew by approximately 43% to reach 183 million metric tonnes, with palm oils also representing 35% of the global volume registered in 2017 (USDA, 2017; USDA, 2016).

In this context, the current demand for vegetable oils is assumed to be driven by food consumption and first-generation biofuels production (Rulli et al., 2016; Plath et al. 2016). Besides contributing to sustaining high food prices worldwide, the use of edible parts of food crops for energy production becomes one of the main ethical conflicts among food security, bioenergy and natural resource management (Nuffield, 2011; Searchinger et al., 2013; FAO, IFAD and WFP, 2015).

Sustainability involves assessing trade-offs among multiple dynamic goals and striving for continual improvement, rather than achieving a particular state. In this sense, many of the issues related to food production may be overcome to promote the use of edible and non-edible vegetable oils as industrial raw materials (Kline et al., 2016). There is, thereby, a clear need for knowledge on new sources of vegetable oils that meet impending food and industry demands around the world (Cardoso et al., 2017; USDA, 2017; FAO, 2016).

Acrocomia aculeata (Jacq.) Lodd. ex Mart, known as macauba (macaw) in Brazil, is an oleaginous palm native to the ecotone area between Cerrado and Amazon rainforest, in tropical America (Uhl and Dransfield, 1987). Being one of the most widespread palms in the Neotropics, it occurs naturally in environments characterised by semi-deciduous forest or savanna as well as in anthropized areas such as deforested sites and pastures (Pires et al., 2013). Like most of the palm trees, macauba requires from 4 to 8 years to initiate fructification. An adult palm fructifies almost the whole year with productivity from 4 to 6 tonnes of esculent oil per hectare (Rettore and Martins, 1983). 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). However, macauba oil exploitation has the advantage of a broader geographical distribution, suiting to edaphoclimatic zones, which feature conditions averse to African palms, such as low water supply, high irradiance, and low fertile soils. Its potential to be incorporated into agrosilvopastoral systems also adds to the sustainability of the productive chain (Lanes et al., 2016). Considering that high yield has been an essential characteristic for the selection of commercial harvests, it has a potential role as an alternative oil crop that deserves further investigation (Rodriguez-Amaya et al., 2008).

Notably, previous studies on the chemical composition of the macauba fruit and oils have mostly focused on the fatty acids profile (Rettore and Martins, 1983; Evaristo et al., 2016; Del Rio et al., 2016; Nascimento et al., 2016). Results related to these studies particularly indicate that the macauba mesocarp represents up to 49% of the total fruit weight (d.b.), which oil content reaches 55% to 69% of the dry matter content. Readily edible, the oil extracted from the fruit mesocarp might be considered a significant tradeoff between degradation resistance and nutritional value because of its high content (up to 67%) of monounsaturated fatty acids (MUFA), mainly oleic acid (Bora and Rocha, 2004; Hiane et al., 2005; Nunes et al., 2015; Trentini et al., 2017). Another characteristic specific of the macauba mesocarp oil is the content of total carotenoids, which can reach up to 378 $\mu g.g^{-1}$ of oil surpassing of other tropical fruits (Nunes et al., 2015; Coimbra and Jorge, 2012; Rufino et al., 2010; Ramos et al., 2008; Rodriguez-Amaya et al., 2008).

Consumers have shown an increasing demand for natural products from the food industry (Cataldo et al., 2016; Babbar et al., 2015, Lim and Kim, 2016). The consumption of these products tends to be associated with the health-related benefits obtained from several classes of bioactive compounds. Monounsaturated fatty acids, as well as of carotenoids, tocopherols, tocotrienols, among other micronutrients, have been related to human blood cholesterol-lowering as well as to reducing the incidence of coronary heart and various other human diseases (Juárez-Hernández et al., 2016; Rodriguez-Amaya et al., 2006; Lescano et al., 2015). Additionally, carotenoids together with tocols (Coimbra and Jorge, 2011), contribute to vegetable oil stability due to their chemical action (antioxidant) and preservation properties (Ciconini et al., 2013; Nunes et al., 2015; Trentini et al., 2017).

Despite the socioeconomic and scientific interests, further research on the composition and processing of *Acrocomia aculeata* is still required (Cardoso et al., 2017). When considering the increasing interest in the edible fruit oils (Nunes et al., 2015; Coimbra and Jorge et al., 2011; Hiane et al., 2005), the physical and chemical characteristics are widely known to vary within different seasons, genotypes and maturation stages, making previous research results difficult to compare (Ciconini et al., 2013; Pires et al., 2013; Rettore and Martins, 1983; Evaristo et al., 2016). This needs to be considered in order to make samples representative of quantitative measurements (Rodriguez-Amaya and Kimura, 2004) and to allow for the correction of harvest and post-harvest handlings (CAC, 2015; Brasil, 2005).

The present study considered the need to characterise the macauba mesocarp oil comprehensively and was undertaken with the objective to build up knowledge that might help to potentially set up standards encompassing the quality, composition and identity characteristics of the edible material. We screened five oil samples mechanically extracted from the mesocarp of the fruit, under the assessment of different temperature and pressing conditions. The resulting data allowed us to select the coldly pressed sample that was complementary characterised. The comparison of the analytical results with previously published data aimed to gather information on quality parameters of the macauba raw material.

4.2 Materials and methods

4.2.1 Fruit sourcing and pre-processing

Macauba fruit was collected from native palms with a maximum of five days after the fall. Geographical coordinates of the palms were recorded based on Lat/Lon-WGS84 geodetic datum. The coordinates 19° 52' 23.1"*S*; 43° 57' 52.9"*W*, 19° 52' 20.4"*S*; 43° 58' 22.5"*W* and 19° 52' 10.0"*S*; 43° 57' 58.0"*W* correspond to the area of the Universidade Federal de Minas Gerais – UFMG, located in the metropolitan region of Belo Horizonte, Minas Gerais, Brazil. Once collected, the fruit was rinsed with tap water, immersed for 5 min in a 2% sodium hypochlorite solution (Gonçalves et al., 2013) and dried at room temperature. The epicarp was then broken to access the mesocarp which was promptly separated from the fresh fruit to produce slices with an average linear dimension of 0.15 m. The storage occurred at a subfreezing temperature (Parducci and Fennema, 1978).

Before the oil extraction, the mesocarp slices were thawed, air dried at 60 °C, until the moisture was below 10% (Silva and Andrade, 2013; Coimbra and Jorge, 2011), and comminuted in an electric grinder coupled to a stainless-steel cup. The raw material (16.3 kg) was stored at refrigeration temperature. The contents (*w/w*, on dry basis) of moisture, protein and ash were of 3.3 ± 0.1%, 6.3 ± 0.1% and 6.2 ± 0.1%, respectively (AOCS, 2009).

4.2.2 Oil Samples: Monitored conditions

The samples hence consisted of virgin edible oil (CAC, 2015) mechanically obtained from the mesocarp of macauba fruit by continuously operated *Expeller*® press. The sampling points were carried out along three subsequent pressings combined with five different sampling temperatures (Table 4.2.2.1). It is worth mentioning that fruit pressing occurred without

temperature supply, being the recorded increase due to heat transfer between the warmer surface of the *Expeller*® press (helical thread, which revolves with concentric friction within a perforated cylindric component) and the macauba mesocarp oil.

Amber glass vials (15 mL) were filled with the samples to the maximum working volume, minimising the impact of light and the risk of oxygen intrusion by reducing the volume of headspace. After sampling, the filled vials were immediately subjected to an ice bath and promptly stored at -18 ºC till the analytical determinations (Pristouri et al., 2010; Parducci and Fennema, 1978).

Table 4.2.2.1. Samples identification: Different pressing-temperature combinations for the collected samples

Sampling Points	Sample ID	Subsequent Pressings	Sampling Temperatures
1	M1	1st Pressing	34 °C
2	M2	1st Pressing	55 °C
3	M3	2nd Pressing	60 °C
4	M4	2nd Pressing	70 °C
5	M5	3rd Pressing	95 °C

4.2.3 Initial step: Sample screenings

Before the analysis, the virgin oil samples, obtained by mechanical procedures, corresponding to the five points (M1, M2, M3, M4 and M5), were centrifuged only (CAC, 2015), at 3300 RPM and 20 °C, for 10 minutes (Paucar-Menacho et al., 2007).

The samples, free of macroparticles (Nunes et al., 2015), were submitted to the following determinations:

- Acid value: AOCS Official Method 3d Cd-63 (AOCS, 2009).
- Oil Stability Index: AOCS Official Method Cd 12b-92 (AOCS, 2009).
- Tocols content: Determined by Ultra High-Performance Liquid Chromatography coupled to Mass Spectrometry (UHPLC/MS), according to an Adapted Methodology previously optimised by Ansolin et al. (2017).

The analytical results were subjected to the analysis of variance. Differences were tested between means at 5% probability (R Core Team, 2016) by Tukey's test.

4.2.4 Cold Pressed oil characterisation

After the screenings, the following physicochemical and quality characteristics were determined for the coldly pressed sample (M1), which showed the highest tocols content, higher oil stability index and a low acid value.

- Iodine Value: AOCS Official Method Cd 1c-85 (AOCS, 2009).
- Peroxide Value: AOCS Official Methods Cd 8b-90 (AOCS, 2009).
- Saponification Value: AOCS Official Method Cd 3-25 (AOCS, 2009).
- Insoluble Impurities: AOCS Official Methods Ca 3a-46(AOCS, 2009).
- Unsaponifiable Matter: AOCS Official Method Ca 6a-40 (AOCS, 2009).
- Relative Density (25 °C): AOCS Ofcial method Cc 10a-25 (AOCS, 2009).
- Kinematic Viscosity (40 °C): ASTM D 2515-66 (ASTM, 2017).
- Mineral Contents: Determined by ICP-OES, according to NBR 15553 (ABNT, 2015).
- Total Carotenoids: Determinations of total carotenoids occurred using a Hach DR 2800 UV/VIS-spectrophotometer (Hach, Loveland, CO, USA) as recommended by Rodriguez-Amaya and Kimura (2004) and suggested by PORIM (1990). An absorption coefficient ($A_{1\ cm}^{1\%}$) of 2580 in high purity n-hexane was considered and the peaks were detected at 450 nm (Zscheile et al., 1942).

The fatty acids essential composition was analysed as follows.

- Fatty Acids Composition: The procedure applied for determining the essential composition of fatty acids was adapted from a method previously optimised by Christie (1989) and Guo et al. (2011). The analysis was carried out on a GC-2010 System (Shimadzu, Japan) fitted with a Flame Ionisation Detector and equipped with auto-sampler (1µl / split: 1/50). Operating conditions included injector and detector temperatures both at 260°C, and H_2 as the carrier gas (linear velocity: 20 $cm.s^{-1}$). Separation was achieved on a SP2340 capillary column (60 m x 0,25 mm x 0,20 µm). The oven temperature started at 140 °C for 5 min, increased by 4 $°C.min^{-1}$ to 240 °C when was held for 19 min. Quantification of individual fatty acid methyl esters – FAME considered a standard mixture of 37 esters of fatty acids (Supelco, Bellefonte, Pa., USA), C4:0 to C24:1 (purity > 99.1%).

4.3 Results and discussion

4.3.1 Screened samples

Table 4.3.1.1 shows the mean and standard deviation for the five screened samples, free of macroparticles, submitted to the determinations of Acid Values, Oil Stability Indexes and Tocols contents.

Table 4.3.1.1. Screened samples of macauba oil mechanically extracted from the fruit mesocarp under subsequent pressing conditions

Determinations (± SD)[1]		Samples				
		M1	**M2**	**M3**	**M4**	**M5**
Acid Value (mg KOH.g^{-1})		1.6 ± 0.1^{a}	1.7 ± 0.2^{a}	1.7 ± 0.2^{a}	1.7 ± 0.1^{a}	1.8 ± 0.1^{a}
Acid Value (% oleic acid)		0.8 ± 0.1^{a}	0.8 ± 0.1^{a}	0.8 ± 0.1^{a}	0.8 ± 0.1^{a}	0.9 ± 0.1^{a}
Oil Stability Index (hours)		6.4 ± 1.1^{a}	5.2 ± 0.0^{a}	3.8 ± 0.1^{b}	3.8 ± 0.1^{b}	3.3 ± 0.0^{b}
Tocols (mg.kg^{-1})	ɣ-Tocotrienol	11.2 ± 0.1^{a}	10.3 ± 0.0^{b}	10.2 ± 0.2^{b}	9.8 ± 0.1^{c}	9.2 ± 0.1^{d}
	α-Tocotrienol	29.7 ± 0.1^{a}	27.1 ± 0.1^{b}	24.5 ± 0.1^{c}	22.3 ± 0.1^{d}	20.2 ± 0.0^{e}
	α-Tocopherol	44.6 ± 0.3^{a}	43.3 ± 0.4^{b}	38.7 ± 0.3^{c}	36.5 ± 0.1^{d}	33.4 ± 0.1^{e}
	Total	85.5 ± 0.2^{a}	80.7 ± 0.3^{b}	73.4 ± 0.4^{c}	68.6 ± 0.0^{d}	62.8 ± 0.1^{e}

[1]*The results represent the mean ± standard deviation of the analysis performed in triplicate. a, b,c,d,e (column) - means, followed by the same letter, do not differ by Tukey's test (P < 0.05).*

As it can be observed, there was no significant statistical difference between the acid values among the analysed samples. Importantly, the contents of free fatty acids – FFA were well bellow the regulatory limits of up to 4 mg KOH.g^{-1} for virgin oils for human consumption (CAC, 2015; MAPA, 2006; Brasil, 2005). Also, the acid value (0.8%, oleic acid) was below the acceptable limit of 3% economically applied for palm oils, what raises the prospects of utilising *Acrocomia aculeata* as an alternative source of high-quality raw material, for multi-purpose employments (Nunes et al., 2015).

It is known that decompositions of triglycerides are catalysed by lipolytic enzymes, which are effective in accelerating the formation of FFA in the macauba oil (Coimbra and Jorge 2011). This reaction can be favoured by injury of falling fruit and accelerated by heat and light (Parducci and Fennema, 1978). It should thus be considered that once a high acid value is recorded for the macauba mesocarp oil, it may be caused by mismanagement of the fruit, from harvest to oil extraction. Rettore and Martins (1983) accordingly reported a 45-fold increase in the acidity of macauba mesocarp oils when the raw materials were exposed to adverse storage conditions. The same authors observed lower percentages of free oleic acids (0.4%) for fresh fruit when processed

immediately after collection. Evaristo et al. (2016) stated an increase of up to 47% in the FFA for the macauba mesocarp oil when upon inadequate storage conditions and continuous fruit-ground contact, irrespective of fungicide application. Cavalcanti-Oliveira et al. (2015) pointed out that the harvest of macauba fruit without contact with the ground can be stored for up to 15 days, without exceeding 4% of acidity, when conserved into in acid solutions.

In this sense, the fruit harvest and post-harvest handling adopted in the present study may have been an important factor to avoid intense hydrolysis reaction of the triglycerides in the mesocarp oil, helping to keep the relatively low acidity of the samples, consequently increasing the Oil Stability Index – OSI (Sánchez-Moreno et al. 2006). Although a decrease is in general observed for the oil stability times, that is in parallel with a relative increase in the acid values (Kiritsakis et al., 2002), the determined OSI does not differ significantly between the screened samples, except when comparing samples obtained by first (M1 and M2) and subsequent pressings (M3, M4 and M5). This indicates the resistance towards degradation, which may be likewise related to the mono-unsaturated composition of fatty acids in the mesocarp oil, as discussed later in this paper.

The naturally present tocols in the macauba mesocarp oil may either have contributed to the stability of the samples due to their chemical action (antioxidant) and preservation properties (Decker et al., 2005). Along with the extraction, losses of up to 27% for tocol homologues (85.5 to 62.8 $mg.kg^{-1}$) indicated that increases in temperature might have activated oxidant reactions. A significant variation of around 18%, 32% and 25% was observed in the contents of ɣ-tocotrienol, α-Tocotrienol and α-tocopherol, respectively, during the processing. The higher retention of α-Tocopherol as compared with α-Tocotrienol could correspond to an increase of antioxidant activity (Sookwong et al., 2010).

Sample M1 presented the highest amounts ($mg.kg^{-1}$) of α-Tocopherol (44.6 ± 0.3), α-Tocotrienol (29.7 ± 0.1) and ɣ-Tocotrienol (11.2 ± 0.1), which were within the same range as other vegetable oils including coconut oil, sesame seed oil, palm kernel stearin and palm kernel olein (CAC, 2015). Besides the health benefits, the identification of tocotrienols in the oil stands out as the compound is closely related to the vitamin α-Tocopherol.

4.3.2 Cold pressed oil

Based on the screenings, the coldly pressed sample (M1), which showed the highest tocols content (85.5 $mg.kg^{-1}$), higher oil stability index (6.4 hours) and a low acid value (1.6 $mg\,KOH.g^{-1}$),

was then characterised. Table 4.3.2.1 thereby presents the mean and standard deviations for the measured quality characteristics of the macauba mesocarp oil allowing the comparison with levels employed by the Codex Standard 210-1999, for cold pressed and virgin edible oils. While those levels are recommendations for voluntary application by members, Codex Standards have in many cases served as the basis for several national legislations contributing to the safety, quality, and fairness of international food trades (CAC, 2015; Brasil, 2005).

Table 4.3.2.1. Quality characteristics of the coldly pressed macauba oil

Quality Characteristics	Macauba mesocarp oil Values (± SD)[a]	Cold Pressed and Virgin Oils Maximum Levels (CAC, 2015)
Peroxide Value (meq O_2.kg^{-1})	13.70 ± 0.08	15.00
Insoluble impurities (% *w*/*w*)	0.04 ± 0.01	0.05
Iron (mg.kg^{-1})	0.78 ± 0.18	5.00
Zinc (mg.kg^{-1})	0.61 ± 0.12	N/A[b]
Potassium (mg.kg^{-1})	23.60 ± 0.07	N/A[b]
Calcium (mg.kg^{-1})	30.55 ± 0.71	N/A[b]
Magnesium (mg.kg^{-1})	27.15 ± 0.49	N/A[b]
Phosphorus (mg.kg^{-1})	69.75 ± 0.64	N/A[b]
Sodium (mg.kg^{-1})	1.35 ± 0.07	N/A[b]

[a]*Standard Deviation*
[b]*N/A - Not Applicable*

As can be seen from Table 4.3.2.1, the peroxide value (13.7 meq O_2.kg^{-1}) and the insoluble impurities (0.04%) determined for the evaluated macauba mesocarp oil conform to those recommended by the Codex Alimentarius. Values that are below the maximum specified are in compliance with the Standard (CAC, 2015). The peroxide value represented the total hydroperoxide content in the oil which determination is most widely used for evaluating edible oil quality. Once the peroxide decomposition is one of the primary practical sources of initiators for oxidations in vegetable oils (Macfarlane et al., 2001), the more reduced the initial value, the lower may be the potential concentrations of peroxyl radicals that could degrade the macauba mesocarp oil.

Regarding the presence of trace metals, the redox metal ions such as Fe^{2+}/Fe^{3+} are active catalysts for which actions might potentially contribute to initiating further autoxidation in vegetable oils (Macfarlane et al., 2001). However, especially for the macauba mesocarp oil, it is observed that the measured concentration of iron (0.78 ± 0.18 mg.kg^{-1}) is well below the maximum value (5.00 mg.kg^{-1}) recommended by the Codex Standard mentioned above.

Moreover, as the concentration of transition metals are in general relatively low in the oil studied, to some extent, they are not expected to interfere with potential rancidity or losses of antioxidant compounds. The relatively high amount of phosphorus in the oil (69.75 $mg.kg^{-1}$) deserves attention. The reported levels may raise the need for physical processes of extraction without permanently diminishing related industrial prospects or a consideration of their nutritional value (O'Brien, 2004).

Regardless of the intended market for the raw material, the compliance to legal standards must be pursued including to guarantee the sustainability of the productive crop chain (Nunes et al., 2015). Considering the significant socioeconomic interest in the edible macauba mesocarp oil (Cardoso et al., 2017), Table 4.3.2.2 presents the fatty acid composition of the studied sample as compared with data obtained from previous studies, as well as with *Elaeis guineensis* oils which stand out as components for the food industry.

Table 4.3.2.2. Fatty acid compositions (expressed as percentages of total fatty acids) of *Acrocomia aculeata* and *Elaeis guineensis* oils

Label	Individual Fatty Acids (%)	*Acrocomia aculeata*		*Elaeis guineensis*		
		Measurements	Ref.[a]	Palm Oil[b]	Palm Olein[b]	Palm Stearin[b]
F8	**n-Octanoic**	0.08 ± 0.05	ND[c] – 0.45	ND[c]	ND[c]	ND[c]
F11	**n-Undecanoic**	0.08 ± 0.04	ND[c]	ND[c]	ND[c]	ND[c]
F12	**n-Dodecanoic**	0.04 ± 0.01	ND[c] – 1.97	ND[c] – 0.5	0.1 – 0.5	0.1 – 0.5
F14	**n-Tetradecanoic**	0.07 ± 0.00	ND[c] – 0.70	0.5 – 2.0	0.5 – 1.5	1.0 – 2.0
F15	**n-Pentadecanoic**	0.17 ± 0.00	ND[c] – 0.08	ND[c]	ND[c]	ND[c]
F16	**n-Hexandecanoic**	19.62 ± 0.56	13.26 – 27.77	39.3 – 47.5	38.0 – 43.5	48.0 – 74.0
F17	**n-Heptadecanoic**	0.09 ± 0.00	ND[c] – 1.15	ND[c] – 0.2	ND[c] – 0.2	ND[c] – 0.2
F18	**n-Octadecanoic**	5.15 ± 0.17	1.08 – 5.92	3.5 – 6.0	3.5 – 5.0	3.9 – 6.0
F20	**n-Eicosanoic**	0.21 ± 0.00	ND[c] – 0.50	ND[c] – 1.0	ND[c] – 0.6	ND[c] – 1.0
F22	**n-Docosanoic**	0.14 ± 0.01	ND[a]	ND[c] – 0.2	ND[c] – 0.2	ND[c] – 0.2
∑ SFA		**25.65 ± 0.84**	**18.55 – 29.35**	**43.3 – 57.4**	**42.1 – 51.5**	**53.0 – 83.9**
F16:1	**(Z)-Hexadec-9-enoic**	1.68 ± 0.04	ND[c] – 5.21	ND[c] – 0.6	ND[c] – 0.6	ND[c] – 0.2
F17:1	**(Z)-Hepta-10-enoic**	0.06 ± 0.00	ND[c] – 0.11	ND[c]	ND[c] – 0.1	ND[c] – 0.1
F18:1	**(Z)-Octadec-9-enoic**	60.33 ± 1.18	52.57 – 65.87	36.0 – 44.0	39.8 – 46.0	15.5 – 36.0
F20:1	**(Z)-Eico-11-enoic**	0.07 ± 0.01	ND[c] – 0.14	ND[c] – 0.4	ND[c] – 0.4	ND[c] – 0.4
∑ MUFA		**62.14 ± 1.23**	**56.84 – 66.88**	**36.0 – 45.0**	**39.8 – 47.1**	**15.5 – 36.7**
F18:2	**(Z,Z)-Octadec-9,12-enoic**	8.81 ± 0.32	3.90 – 17.70	9.0 – 12.0	10.0 – 13.5	3.0 – 10.0
F18:3	**(Z,Z,Z)-Octadeca--9,12,15-trienoic**	0.73 ± 0.02	ND[c] – 6.81	ND[c] – 0.5	ND[c] – 0.6	ND[c] – 0.5
F20:2	**(Z,Z)-Eicosa-11,14-dienoic**	1.83 ± 0.46	ND[c] – 2.26	ND[c]	ND[c]	ND[c]
∑ PUFA		**11.37 ± 0.80**	**4.80 – 19.20**	**9.0 – 12.5**	**10.0 – 14.1**	**3.0 – 10.5**

[a]References: Rettore and Martins (1983), Bora and Rocha (2004), Hiane et al. (2005), Coimbra and Jorge (2011), Nunes et al. (2015), Del Rio et al. (2016), Trentini et al. (2017)
[b]According to CAC (2015).
[c]*ND - Non-detectable, defined as ≤ 0.05%*

The average composition of fatty acids in the macauba mesocarp oil is mostly oleic acid (60.33%) and palmitic acids (19.62%). From the perspective of industrial applications, a brief discussion could arise regarding remarkable efforts in the sense of producing blends of vegetable oils also to enhance the nutritional characteristics of structured lipids with specific functional properties (Hashempour-Baltork et al., 2016; Moreira et al., 2017; Şahin-Yeşilçubuk and Akoh et al., 2017).

The predominance of oleic and palmitic acids in the macauba oil opens perspectives for new products and processes development (Xie and Qi, 2014; Gibon and Kellens, 2014; Xie et al., 2015). The use of *Acrocomia aculeata* oil can be extended by the use of techniques such as crystallisation from the melt, from which high-melting solid phase (around 25%), and low-melting liquid phase (around 62%), particularly rich monounsaturated fatty acids (MUFA), could be rendered (Timms, 2005).

Table 4.3.2.2 shows the predominance of MUFA in the crude macauba oil (62.14%), similar to those verified in other edible oils rich in these fatty acids, such as olive oil (55.0 – 83.0%), peanut oil (15.0 – 47.0%), canola oil (54.0 – 75.0%), and sunflower seed oil (43.1 – 71.8%) (CAC, 2015; CAC, 2013; Hiane et al., 2005). The MUFA content (62.14%) in the present study is higher than that usually found in *Elaeis guineensis* oil, with (36.0 – 44.0), stearin (15.6 – 36.0) and olein (39.8 – 46.0). Similar to palm olein the macauba oil presents a tradeoff between degradation resistance and nutritional value, mainly because of its high oleic acid (ω-9) content (Achir et al., 2010).

Regarding the ω-6 family of fatty acids, the linoleic acid in the macauba mesocarp oil (8.81%) was in the range of those reported for palm oil (9.0 – 12.0%) and palm stearin (3.0 – 10.0%), as well as for sunflower seed oil (2.1 – 17.0%) and virgin and refined olive oils (3.5 – 21.0%). The level was higher than those for palm kernel oil (1.0 – 3.5%), palm kernel olein (2.4 – 4.3%) and palm kernel stearin (0.5 – 1.5%). The level of polyunsaturated fatty acids (PUFA) determined (11.37%) is in the range of *Elaeis guineensis* oils again evidencing the potential of *Acrocomia aculeata* as an alternative feedstock for industrial purposes (CAC, 2015).

The Joint FAO/WHO Expert Consultation on Fats and Oils in Human Nutrition (Uauy et al., 2009) recommend governments worldwide to take steps to support the use of alternative vegetable oils rich in MUFA and PUFA with a substantial gain for the health of the global population.

The degrees of unsaturations in the macauba mesocarp oil are coherently supported by the iodine and saponification values also determined (see Table 4.3.2.3).

Table 4.3.2.3. Chemical and physical characteristics of macauba mesocarp oil as compared with previous determinations from literature

Chemical and Physical Characteristics	Macauba mesocarp oil		
	Determinations (± SD)[b]	Previous Studies	Ref.[a]
Iodine Value (g I_2.100 g^{-1})	73.9 ± 1.74	75.4 – 85.8	1,2,3,4,9,11
Saponification Value (mg KOH.g^{-1})	123.5 ± 5.2	158.0 – 210.5	1,2,3,4,6,7,9,11
Refractive Index (40 °C)	N/A[c]	1.4427 – 1.4662	1,2,3,1
Kinematic viscosity as 40 °C (cSt)	41.7 ± 0.0	35.0 – 44,5	8,9,10
Relative density (25 ºC/20 ºC)	0.9172	0.9036 – 0.9256	1,2,6,7,8
Unsaponifiable Matter (%)	1.5 ± 0.0	0.4 – 0.9	1,4,6
Total Carotenoids	248.0 ± 8.0	300 – 378	5,6

[1]Rettore and Martins (1983), [2]Bora and Rocha (2004), [3]Hiane et al. (2005), [4]Coimbra and Jorge (2011), [5]Coimbra and Jorge (2012), [6]Nunes et al. (2015), [7]César et al. (2015), [8]Da Conceição et al. (2016), [9]Silva et al. (2016), [10]Prado et al. (2016), [11]Souza et al (2016).
[b]Standard Deviations
[c]*N/A - Not Applicable*

It is noted from Table 4.3.2.3 that the iodine value determined for the coldly pressed sample (73.9%) to some extent agree with the range registered in previous studies on the macauba oil, accordingly suggesting high degrees of unsaturations (Coimbra and Jorge, 2011; Bora and Rocha, 2004; Hiane et al., 2005; Rettore and Martins, 1983; Silva et al., 2016; Souza et al., 2016). The saponification value analysed for the macauba mesocarp oil is shown to be lower than the levels also stated from Coimbra and Jorge (2011), Nunes et al. (2015), Bora and Rocha (2004), Hiane et al. (2005), Rettore and Martins (1983), César et al. (2015), Silva et al. (2016) and Souza et al (2016). Nevertheless, although geographical and climatic variations may affect the technological characteristics of edible vegetable oils (CAC, 2015), the present results extend the range of values found previously. As generally longer chain fatty acids are related to lower saponification values, relatively higher amounts of shorter chain fatty acids might be found with the higher concentrations of palmitic (27.77%), palmitoleic (5.21%) and lauric (1.97%) acids from Trentini et al. (2017), Coimbra and Jorge (2011), Hiane et al. (2005) and Del Rio et al. (2016).

The refractive index – RI (40 °C) ranges reported may be employed as an identity parameter specific of the *Acrocomia aculeata* oil. This parameter is dependent on the oil molecular weight, fatty acid chain length, degree of unsaturation, and degree of conjugation. Coupland and McClements (1997) pointed out that values of RI for vegetable oils should be between 1.447 and 1.482, in accordance with the presented data. The levels determined in for the kinematic viscosity at 40 °C (41.7 cSt) and relative density (0.9172) fall within the range presented.

It is widely known that the viscosity of liquid oils is dependent on the fatty acid composition being also influenced by temperature. Similarly, the density of vegetable oils depends on their fatty acids, the temperature and other minor components. Overall, it becomes necessary to emphasise that, the monitoring of these physical parameters comes to be essential to evaluate the quality of vegetable oils. Oxidative changes of fatty acids tend, for instance, to promote decreases in total unsaturation and increases in the free fatty acids content, with similar variations in the values of RI, density and viscosity (Perkins, 1992; Timilsena et al., 2017).

The value of unsaponifiable matter (1.5%) determined in this study equals the maximum level established by the Codex Alimentarius Commission for olive oils (CAC, 2013), soybean oil, sunflower seed oil and coconut oil (CAC, 2015), all suitable for human consumption. This values are slightly higher than the corresponding maximum values registered for babassu oil and palm oil (1.2%), palm stearin (0.9%), palm olein (1.3%) and lower than that for value maize oil (2.8%) (CAC, 2015; O'Brien, 2004). Values obtained for the parameter in vogue are usually presented at less than 2.0% in vegetable oils (Shahidi and Shukla, 1996), which is consistent with our observations.

The crude macauba mesocarp oil contains high amounts tocopherols, tocotrienols, phytosterols and other carotenoids. The identification of the closely related compounds α-Tocotrienol (29.7 $mg.kg^{-1}$), ɣ-Tocotrienol (11.2 $mg.kg^{-1}$) and α-Tocopherol (44.6 $mg.kg^{-1}$) have been already discussed as the compounds stand out in the oil evaluated. Also, the mesocarp oil showed relatively high amounts of total carotenoids (248 ± 8 $mg.kg^{-1}$) which are similar to the findings of Coimbra and Jorge (2012) and Nunes et al., (2015), who reported the crude macauba oil to contain 300-378 $mg.kg^{-1}$ of these natural tetraterpenoids. Although some variability can be observed, it is suggested that the slight reduction in the studied sample may also be related to the pre-processing step adopted in the present study.

Accordingly to Rodriguez-Amaya (2008) and Rufino et al. (2010), the contents of carotenoids in the mesocarp of *Acrocomia aculeata* surpasses of other tropical fruits. Therefore, it becomes one of its remarkable characteristics also contributing with evidences that products derived from macauba may have a good consumer acceptance competing against products that don't have that nutraceutical value and natural appeal (Palmero et al., 2013; Lim and Kim, 2016; Cataldo et al., 2016; Babbar et al., 2015).

The highly unsaturated structures of carotenoids are, on the one hand, responsible for their functional properties. On the other hand, the correlated significant numbers of double bonds in the compounds molecule creates stability challenges (Knockaert et al., 2012; Lemmens et al.,

2011). As a result of exposure to high temperature, light and pro-oxidant agents, carotenoids are expected to undergo degradation and isomerisation (Rodriguez-Amaya et al., 2008; Sampaio et al., 2013) which changes should be prevented to maintaining biological activities.

As an essential unity operation, thermal processings may likewise influence both the carotenoids bioaccessibility (Lemmens et al., 2011; Palmero et al., 2013) and the health-related attributes of macauba mesocarp oil (Rodriguez-Amaya et al., 2006; Nunes et al., 2015; Hiane et al., 2005; Magosso et al., 2016). Future research encompassing the assessment of the thermal effects on the bioactives of macauba oil, including carotenoids, tocols and fatty acids, among other micronutrients, require further investigation and might help food processing research to define appropriate ways to process the feedstock without affecting these natural constituents (Hanna et al., 2017; Ogan et al., 2017; Fogler 2016).

4.4 Conclusions

This is the first report on the assessment of different mechanical extractions conditions to obtain high-quality crude macauba mesocarp oil. The harvest and post-harvest handling and pre-processing steps have been indicated to be major factors in avoiding hydrolysis of the triglycerides in the mesocarp oil, contributing to maintain the relatively low acidity of the samples. This supports the feasibility of commercial exploitation of high-quality macauba mesocarp oil as a convenient source of raw material for multi purposes, including food processing. For as much as macauba fruit stills tend to be processed by equipment originally designed for other biomasses, the currently deployed infrastructures in the productive crop chain acknowledge customisations for increasing quality and efficiency. The oil extracted from the macauba mesocarp may be considered a significant tradeoff between degradation resistance and nutritional value because of its high content of monounsaturated fatty acids (MUFA), mainly oleic acid. The obtained results contribute to the evidence that products derived from macauba may have a good consumer acceptance competing against products that don’t have that nutraceutical value and natural appeal. The conducted survey strengthens the need for continuously building up knowledge that can help to set up standards encompassing the quality, composition and identity characteristics of the macauba mesocarp oil. It is suggested that the compliance to legal standards must be continuously pursued to guarantee the sustainability of the productive crop chain. Summarily, the study inspires further research on food processing, which is required to define appropriate ways to process the raw material without affecting the natural constituents.

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CHAPTER 5. Thermal Degradation Kinetics: Carotenoids Influencing Macauba Mesocarp (*Acrocomia aculeata*) Oil attributes

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Abstract

In the present work, the kinetics of β-carotene and β-cryptoxanthin were investigated in edible oil mechanically extracted from the mesocarp of macauba (*Acrocomia aculeata*) fruit. The crop has a similar productive potential to African palm (*Elaeis guineensis*) which is among the highest oil-yielding plants in the world. The heating process was conducted under a nitrogen atmosphere, without exposure to light. Heat treatments were assumed isothermal and performed at five different temperatures, ranging from 110 to 150 °C. HPLC analyses were carried out in addition to spectrophotometric determinations to monitor the carotenoids variations over the heating time. The initial composition of the oil was also highlighted for tocols, peroxide and trace metals contents. Thermodynamic parameters were obtained from the expression of rate constant derived from transition state theory. The results indicated that the first-order kinetic model is appropriate for describing the oxidative degradation of the compounds in the macauba oil. The carotenoids concentrations decreased for all the treatments as a function of heating time becoming faster at higher temperatures. It was determined a definite influence of temperature on the oxidant reactions rates of β-carotene and β-cryptoxanthin, based on the Arrhenius model. The apparent activation energy estimated for β-cryptoxanthin (87 kJ.mol^{-1}) was higher as compared to β-carotene (80 kJ.mol^{-1}) and the sum of β-carotene + β-cryptoxanthin (84 kJ.mol^{-1}). The correlated combinations of k_{ref} and E_a indicate that the kinetic parameters estimated for overall carotenoids might predict the retention of the individual compounds with relative accuracy in the context of industrial scale processes.

Keywords: carotenoids, thermal degradation, kinetics, vegetable oil, macauba

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5.1 Introduction

There is a need for knowledge on new sources of vegetable oils that meet impending food industrial demands around the world. According to the Food and Agriculture Organization of the United Nations, the world population will be greater than nine billion people in 2050. The need for 70% additional food will be disproportionately larger than the predicted 34% increase in population, to meet this demand (Searchinger et al., 2013; FAO, 2016).

Sustainability involves assessing trade-offs among multiple dynamic goals and striving for continual improvement, rather than achieving a specific state. In this sense, the use of edible parts of food crops for energy production is one of the central ethical conflicts related to the complex interactions among food security, bioenergy and resource management (Rulli et al., 2016; Kline et al., 2017). Successful synergies in the current scenario require a focus on specific contextual problems and opportunities. There is thus a need for overcoming many of the issues related to food production, promoting the use of edible and non-edible vegetable oils as essential commodities for the global economy (Plath et al. 2016; USDA, 2017).

Acrocomia aculeata (Jacq.) Lodd. ex Mart known as macauba in Brazil is an oleaginous palm native to tropical America. Being one of the most widespread palms in the Neotropics, it occurs naturally in environments characterised by semi-deciduous forest or savanna as well as in anthropized areas such as deforested sites and pastures (Uhl and Dransfield, 1987). The crop has a similar productive potential to African palm (*Elaeis guineensis*) which is among the highest oil-yielding plants in the world (Evaristo et al., 2016). Macauba, however, has the advantage of being suited to edaphoclimatic zones, which feature conditions averse to African palms, such as low water supply, high irradiance, and low fertile soils (Lanes et al., 2016).

An adult macauba palm fructifies almost the whole year with productivity from 4 to 6 tonnes of esculent oil per hectare (Pires et al., 2013). Considering that high yield has been a primary criterion for commercial harvests selection (Rodriguez-Amaya et al., 2008), these facts already render it an important role as an alternative oil crop. Regarding the macauba mesocarp, which oil content reaches 55% to 69% of the dry matter, it is readily edible and represents up to 46% of the total fruit weight (d.b.). The mesocarp oil has a predominance of unsaturated fatty acids (74%) of which 52% are oleic (ω-9) and 14% linoleic (ω-6) (Coimbra and Jorge, 2011).

Recently, consumers have shown an increasing demand for natural products from the food industry (Cataldo et al., 2016; Babbar et al., 2015). The health-related benefits associated with the consumption of these products are also attributed to the presence of bioactive compounds,

among which micro-nutrients form an important class. In this framework, carotenoids are a group of natural food pigments broadly distributed in nature being also notable for the contribution to the nutraceutical value of several fruits, vegetables, and vegetable oils (Rodriguez-Amaya et al., 2008; Palmero et al., 2013).

The natural carotenoid content in macauba surpasses of other tropical fruits becoming one of its striking characteristics (Rufino et al., 2010; Rodriguez-Amaya et al., 2008). The β-carotene and β-cryptoxanthin respectively represent around 90% and 8% of up to 378 $\mu g.g^{-1}$ of the total carotenoids content in the macauba mesocarp oil (Nunes et al., 2015; Coimbra and Jorge, 2012). In this sense, products derived from macauba may have a good consumer acceptance competing against products that don't have that natural appeal. Besides the health-related benefits, carotenoids can quench singlet oxygen or interact with free radicals (Magosso et al., 2016). Therefore, together with tocols (Coimbra and Jorge, 2011), the mentioned tetraterpenoids contribute to the stability of macauba mesocarp oil due to their chemical action (antioxidant) and preservation properties (Rodriguez-Amaya et al., 2006).

From the perspective of thermal food processing, it is noteworthy that the all-*trans*-carotenoid present in the macauba is the thermodynamically most stable form in nature (Knockaert et al., 2012). The highly unsaturated structures of carotenoids include significant numbers of double bonds which make the compounds considerably sensitive to thermal degradation reactions. Indeed, the rates of the degradation reactions tend to dramatically increase during thermal treatments varying as temperature rises (Achir et al., 2011). Carotenoids losses during food processing have been reported and quantified (Mader, 1964; Onyewu et al., 1986; Palmero et al., 2013) not often encompassing the effects of the processing factors on the thermal degradation.

Accurate knowledge on thermal degradation kinetic is needed to predict specific changes that occur after food processing quantitatively. In this sense, process optimisation requires product-specific kinetic data. Kinetic models are usually supplemented with thermodynamic information for becoming wide applicable in industrial scale. Particularly in engineering, kinetic data is used for designing efficient processes and large scale reactors (Fogler, 2016).

Only a few kinetic parameters are usually available to assess the thermal degradation of β-carotene in real food systems, with less evidence available for characterising the thermal degradation of β-Cryptoxanthin. Previous kinetic evaluation of carotenoids degradation in vegetable oil indicates a first-order reaction kinetic mechanism (Knockaert et al., 2012; Aparicio-Ruiz et al., 2011). The disappearance of β-carotene has also been described by fractional reaction orders bigger than 1 (Sampaio et al., 2013). The analysis of the available kinetic data indicates

that carotene degradation is complex being highly dependent on factors linked to the food systems and the matrix they are studied (Colle et al., 2013; Achir et al., 2010).

It is reasonable to observe the potential opportunities for exploiting thermal degradation kinetics of carotenoids as bioactive compounds in the macauba mesocarp oil. Thus, the present study was undertaken with the primary objective to develop the kinetic modelling involving the thermal degradation of natural carotenoids in the macauba oil. A second objective was to compare the correlated combinations of k_{ref} and E_a statistically for the reactions studied. Additionally, thermodynamic parameters were considered to examine if the studied reactions could potentially proceed through similar mechanisms in the macauba mesocarp oil.

5.2 Materials and methods

5.2.1 Fruit sourcing and pre-processing

Macauba fruit was collected from native palms with a maximum of five days after the fall. Geographical coordinates of palms were recorded based on Lat/Lon-WGS84 geodetic datum. The coordinates 19° 52' 23.1"*S*; 43° 57' 52.9"*W*, 19° 52' 20.4"*S*; 43° 58' 22.5"*W* and 19° 52' 10.0"*S*; 43° 57' 58.0"*W* correspond to the area of the Universidade Federal de Minas Gerais, located in the metropolitan region of Belo Horizonte, Brazil. The macauba mesocarp was promptly separated from the fruit to produce slices with an average linear dimension of 150 mm. Before the oil extraction, the mesocarp was thawed, air dried at 60 °C for 48 hours and comminuted in an electric grinder coupled to a stainless steel cup. The contents of moisture, protein, and ash (*w/w*, on dry basis) for the mesocarp submitted to the oil extraction were of 3.3 ± 0.1%, 6.3 ± 0.1% and 6.2 ± 0.1%, respectively (AOCS 2009).

5.2.2 Oil Samples: Macauba mesocarp oil

The samples consisted of edible oil (kinematic viscosity at 40 °C: 41.7 ± 0.7 $mm^2.s^{-1}$; acid value: 1.6 ± 0.1 mg $KOH.g^{-1}$) mechanically obtained from the macauba mesocarp by continuously operated *Expeller*® press, at 34 °C. The oil yield was 45.1% (*w/w* dried material). The initial peroxide value in the crude oil was of 13.7 meq $O_2.kg^{-1}$. The contents of trace metals ($mg.kg^{-1}$) were of 0.78 ± 0.20 (Iron), 0.61 ± 0.12 (zinc), 23.60 ± 0.71 (potassium), 30.60 ± 0.49 (calcium), 27.15 ± 0.64 (magnesium) and 69.15 ± 1.20 (phosphorus). The insoluble impurities, saponification value and unsaponifiable matter were of 0.04 ± 0.01 (% *w/w*), 120.0 ± 1.2 (mg $KOH.g^{-1}$) and 14.6 ± 0.3 ($g.kg^{-1}$), respectively (AOCS, 2009). Amber glass vials (15 mL) were

filled to the maximum working volume with the oil, minimising the impact of light and the risk of oxygen intrusion by reducing the volume of headspace. Samples were stored at freezing temperature until the thermal treatment.

5.2.3 Thermal treatment

Heating homogeneity was achieved on a dry thermo-block (SAE 1020 steel Dry-Block - CE-350; Cienlab). Aliquots of oil (2000 µL) were placed into glass vials and inserted into the reactor. The vials headspace were flushed with nitrogen gas before heating to avoid the carotenoid oxidation by oxygen intrusion. 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 µL of oil. The whole device was covered with aluminium foil to prevent carotenoid degradation by light.

The thermal degradation kinetics was carried out employing at least five time sampling points, at five temperatures. The different time-temperature combinations are shown in Table 5.2.3.1. After processing for the desired time, the samples were removed from the reactor and immediately subjected to an ice bath to be stored at -18 ºC till the analysis.

Table 5.2.3.1. Thermal treatment for the mesocarp oil: time-temperature combinations.

Temperature Settings (°C)	Time (min)
100	0, 120, 300, 720, 1144, 1530
110	0, 60, 180, 360, 600, 900, 1440
130	0, 30, 60, 100, 150, 270
140	0, 20, 40, 60, 90, 130, 160
150	0,10, 20, 40,60, 100, 120

5.2.4 Carotenoids Analysis

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 of β-carotene and β-cryptoxanthin. Peaks were detected at 455 nm. The separation was achieved at 30 °C using a normal phase column (Phenomenex Luna Silica 2 100A Si: 250 mm × 4.6 mm i.d., 5 µm 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 till 26 min. After every 10 injections of 20 µL, the column was reactivated with a solution of 10% isopropyl alcohol in n-hexane (*v/v*). The carotenoids were identified by the combined use of their relative retention times and previously published UV/Vis spectra (Panfili et al., 2004; Rodriguez-Amaya and Kimura, 2004; Aparicio-Ruiz et al., 2011). The concentrations (mg.kg^{-1}) were expressed based on external matrix calibration (Sigma-Aldrich Corp., St. Luis, Mo., U.S.A.). The spectrophotometric determination of total carotenoids (SD-TC) occurred using a Hach DR 2800 spectrophotometer (Hach, Loveland, CO, USA) as suggested by PORIM (1990). The quantification (mg.kg^{-1}) considered an absorption coefficient ($A^{1\%}_{1cm}$) of 2580 in high purity n-hexane (Zscheile et al., 1942).

5.2.5 α-Tocopherol and α-Tocotrienol analysis

The method 2.432 of the IUPAC (IUPAC, 1987) was applied for the analysis of α-Tocopherol and α-Tocotrienol in the macauba mesocarp oil. Samples were dissolved in n-hexane and directly injected into the HPLC column (Phenomenex Luna Silica (2) 100A Si: 250 mm × 4.6 mm i.d., 5 µm particle size). The analyses were also carried out on the referred Shimadzu system being the tocols separation achieved at 30 °C. A fluorescence detector (RF-20A) was set at 290 nm of excitation and 330 nm of emission to analyse the chromatograms. The mobile phase was n-hexane/isopropyl alcohol (99.5:0.5 *v/v*), and the flow rate was 1.0 mL.min^{-1}. The elution remained isocratic till 14 min after when the eluent composition was 97% A and 3% B till 23 min. The post run time was 14 min. The concentration (mg.kg^{-1}) of α-Tocopherol was expressed by multiplying the corresponding peak area of the chromatograms by a factor previously determined by linear external calibration (Sigma-Aldrich Corp., St. Luis, Mo., U.S.A.). The α-Tocotrienol isomer content was calculated based on the standard peak areas of the related α-Tocopherol analogue.

5.2.6 Kinetic modelling of carotenoids global degradation

The experimental kinetic data is presented in the dimensionless form C/C_0 at different heating time intervals (t), where C is the carotene concentration after a specific heating time interval, and C_0 is the initial amount of carotene in the vials at $t = 0$. The initial degradation rate r (min^{-1}) of each kinetics was found by measuring the slope of the tangent of the curve $C/C_0 = f(t)$ at $t = 0$. For the determination of the activation energies E_a, it was considered the equation (1), which conveys that the degradation rate dC/dt is proportional to the nth power of the carotene

concentration (C in mg.kg^{-1} of oil) at any time t, while k (min^{-1}) is the reaction constant and n is the reaction order.

$$\frac{dC}{dt} = -kC^n \quad (1)$$

With an initial condition where $C = C_0$ at $t = 0$

The rate constants (k) are assumed to vary with the absolute temperature T (K) according to Arrhenius law. Considering the close correlation between k_0 and E_a, a simple reparametrization is achieved by introducing a reference temperature

$$k = k_{ref}\, e^{\left(\frac{-Ea}{R}\left(\frac{1}{T_{(t)}} - \frac{1}{T_{ref}}\right)\right)} \quad (2)$$

In this parametrization, the pre-exponential factor k_{ref} becomes the rate constant at the reference temperature (T_{ref}) of the experiment (chosen as the average of the studied range, 403.15 K). E_a, R, and T are respectively the activation energy (J.mol^{-1}), the gas constant (8.314 J.mol^{-1} K^{-1}) and the oil temperature concerned (K). The units of the specific rate constant and pre-exponential factor vary according to the order (n) of the reactions.

The k value is then replaced in by Eq. (1) and fitted to all the data at once by nonlinear regression (R Core Team, 2016) to estimate an overall k_{ref} and E_a using a numerical solution for the Ordinary Differential Equation to integrate the varying temperature history of each of the experiments (Fogler, 2016). According to Van Boekel (1996), an overall nonlinear regression gives better precision in final estimates than the two-step fitting of the reaction rate constants to the Arrhenius model.

It should be noted that the suitable kinetic model was firstly selected by visual inspection of different concentration plots for the kinetic modelling (Kebede et al., 2015). The model quality was evaluated by scrutiny of residuals and graphically by using the parity plot, showing the relationship between experimental and predicted values (Colle et al., 2013).

The $R^2_{adjusted}$ fitting criteria was also considered in the model selection process according to equation (3).

$$R^2_{adjusted} = 1 - \frac{\left[(DF_{tot} - 1)\left(1 - \frac{SS_{model}}{SS_{total}}\right)\right]}{DF_{error}} \quad (3)$$

In the above equation, DF_{tot} and DF_{error} are a degree of freedom of total and error, respectively, while SS is the sum of squares.

Besides the standard error associated with the estimated parameters k_{ref} and E_a, 90% joint confidence regions (JCR) were constructed to evaluate the statistical confidence of the estimated parameters. The JCR takes into account the correlation between k_{ref} and E_a (Murdoch and Chow, 2013).

The overall disappearances of all β-carotene and β-cryptoxanthin forms were studied to represent the intensity of the carotenoids oxidative reactions (Sampaio et al., 2013; Dhuique-Mayer et al., 2007; Ahmed et al., 2002; Minguez-Mosquera and Jaren-Galan 1995). Oxidation and cleavage products, in addition to 9-*c*is-β-carotene and 13-*cis*-β-carotene isomers, are major carotenoid alterations that occur during food processing. However, the intermediate reaction pathways are supposed to be directly involved in the same type of carotenoid oxidative reactions during heating (Achir et al., 2010).

The kinetic mechanism purposed for the global degradations of β-carotene and β-cryptoxanthin, therefore, considered one step reactions as illustrated in Figure 5.2.6.1

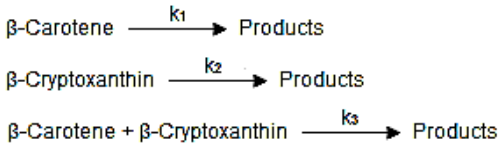

Figure 5.2.6.1. Kinetic mechanisms for thermal degradation reaction of β-Carotene, β-Cryptoxanthin and β-Carotene + β-Cryptoxanthin

5.2.7 Thermodynamic parameters

According to the activation complex theory, enthalpy of activation ($\Delta H^{\#}$) was obtained by regressing ln(k/T) on 1/T, and the entropy of activation ($\Delta S^{\#}$) was obtained from the expression of rate constant derived from transition state theory (Henry et al., 1998).

$$\boldsymbol{ln\left(\frac{k}{T}\right) = \left[\left(ln\left(\frac{k_b}{h}\right)\right) + \left(\frac{\Delta S}{R}\right)\right] - \left[\left(\frac{\Delta H}{RT}\right)\right]} \quad (4)$$

In the above equation, k is the rate constant (at temperature T), k_b is the Boltzmann constant ($1.38064852 \times 10^{-23}$ J.K^{-1}), h the Planck constant ($6.62607004 \times 10^{-34}$ J.s) and R is the universal molar gas constant (8.3145 J.mol^{-1} K^{-1}).

The Gibbs energy of activation can be divided into entropy of activation ($\Delta S^{\#}$) and enthalpy of activation ($\Delta H^{\#}$) by writing:

$$\boldsymbol{\Delta G = \Delta H^{\#} - T\Delta S^{\#}} \quad (5)$$

5.3 Results and discussion

5.3.1 Initial State of macauba mesocarp oil

The analytical measurements of overall carotenoids, tocols content, peroxide value and trace metals are presented in Table 5.3.1.1 to base the kinetic parameterizations in the macauba mesocarp oil better.

Table 5.3.1.1. Initial and final state of the thermally treated mesocarp oil: overall carotenoids, tocols, peroxide value and trace metals.

Oil sample	*t* (min)	Overall crt[b] ± SD[e] (mg.kg^{-1})	Tocols ± SD[e] (mg.kg^{-1})			Peroxide Value (meq O_2.kg^{-1})	Trace metals ± SD[e] (mg.kg^{-1})
			α-T[c]	α-T_3[d]	T[c] + T_3[d]		
MMO[a]	0	248 ± 8	51 ± 3	64 ± 2	115 ± 5	13.7 ± 0.1	Fe: 0.8 ± 0.2
MMO[a] 423.15 K	120	120 ± 1	39 ± 0	49 ± 0	88 ± 1		Zn: 0.6 ± 0.1
MMO[a] 413.15 K	160	129 ± 1	31 ± 4	39 ± 5	70 ± 9		K: 23.6 ± 0.5
MMO[a] 403.15 K	270	132 ± 0	28 ± 4	36 ± 5	65 ± 9		Ca: 30.7 ± 0.5
MMO[a] 383.15 K	1440	112 ± 3	32 ± 3	42 ± 4	74 ± 6		Mg:27.2 ± 0.5
MMO[a] 373.15 K	1534	170 ± 4	37 ± 4	47 ± 6	84 ± 9		P: 69.8 ± 1.5

[a] Macauba mesocarp oil.
[b] β-carotene + β-cryptoxanthin.
[c] α-Tocopherol
[d] α-Tocotrienol
[e] Standard Deviation

Consistent with our observations, Nunes et al. (2015) and Coimbra and Jorge (2012) reported the crude macauba oil to contain 300-378 mg.kg^{-1} of total natural carotenoids. Although some variability is known for different macauba genotypes, the slight reduction observed for the overall carotenoid content (248 ± 8 mg.kg^{-1}) at the start-point of the kinetic may be related to the macauba pre-processing step described in section 2.1. The findings were yet similar to initial levels reported in previous kinetic studies (Zeb and Murkovic 2011; Achir et al., 2010) carried out on carotenoid-enriched vegetable oils.

The initial peroxide value of 13.7 ± 0.1 meq O_2.kg^{-1} conforms to that recommended by the Codex Alimentarius (≤15.0), for virgin oils intended for human consumption (CAC, 2015). Even though the relative importance of peroxides on carotenoids degradation is difficult to determine (Hiatt et al., 1968), this result partially helps to explain why carotenoids degradation occurs even at lower temperatures (Aparicio-Ruiz et al., 2011; Knockaert et al., 2012; Colle et al., 2013). Autoxidation is a free-radical chain reaction, involving a complex series of reactions that initiate, propagate, and terminate the chain. Peroxides are unstable products able to produce free radicals at high temperatures which may further participate in cleavage reactions. It is thus reasonable to

suggest that the peroxide decomposition is one of the primary practical sources of initiators for oxidations in vegetable oils (Macfarlane et al., 2001). Thus, the more reduced the initial peroxide value in macauba mesocarp oil the lower is the potential concentrations of peroxyl radicals that could degrade the highly unsaturated chain of carotenoids.

The presence of trace metals in vegetable oils deserves attention. Particularly, redox metal ions such as Fe^{2+}/Fe^{3+} are active catalysts for which actions also contribute to potentially initiating further autoxidation (Macfarlane et al., 2001). Especially for the macauba mesocarp oil, it is observed that the concentration of iron (0.78 ± 0.20 mg.kg^{-1}) is well below the maximum value (5.00 mg.kg^{-1}) recommended by the Codex Alimentarius (CAC, 2015). It is reasonable to observe that the transition metals present in the oil studied, to some extent, little interfere with reactions. Nevertheless, the actual contribution of the present elements to increases in the nutritional value of the raw material deserves to be emphasised.

It becomes clear that the predominance of unsaturated fatty acids in the macauba mesocarp composition (Coimbra and Jorge 2011) makes the oil also potentially susceptible to oxidation thereby producing radicals (Colle et al., 2013). Perez-Galvez and Minguez-Mosquera (2004) however pointed out that in the absence of oxygen the carotenoid stability tends not to be linked with the unsaturation of the oily system. The present study was conducted under a nitrogen atmosphere and protection from light, therefore, restricting the highly destructive potential of oxygen especially in combination with heat (Rodriguez-Amaya and Kimura, 2004).

In what refers to the tocols content, the findings were consistent with observations by Coimbra and Jorge (2012). Besides the potential health benefits, the identification of α-tocotrienol (64 ± 2 mg.kg^{-1}) stands out as the compound is closely related to α-Tocopherol (51 ± 3 mg.kg^{-1}) playing an important role during the carotenoids degradation. Although a higher retention of α-Tocopherol compared to α-Tocotrienol could correspond to an inverse order of antioxidant activity (Sookwong et al., 2010) the compounds showed similar behaviours.

The effectiveness of antioxidants is dependent on factors such as temperature conditions, stability, physical distribution, mobility in the media, and the presence of synergists or antagonists (Decker et al., 2005). Tocols seemed to be more resistant than carotenoids as also pointed out by Romero et al. (2007). Losses of the tocol homologs observed at the extreme temperatures indicated that oxidant reactions were activated by temperature increases also confirming oxidation reactions along the thermal treatments.

5.3.2 Thermal degradation of carotenoids

Figure 5.3.2.1 illustrates the stability plot for the concentrations of carotenoids during the heating treatment over time. Figure 5.3.2.2 is subsequently presented plotting the experimental levels of carotenoids (expressed normalised) *vs.* the respective predicted levels of the overall model.

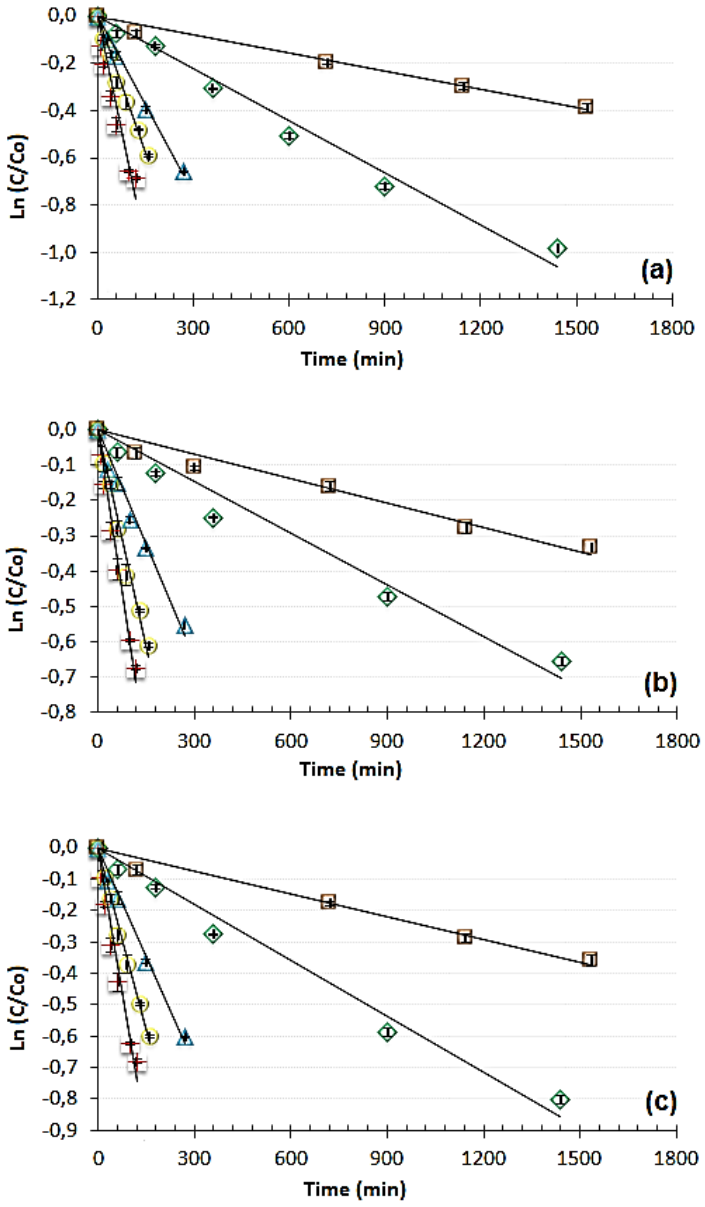

Figure 5.3.2.1. Degradation kinetics plot of carotenoids in macauba mesocarp oil: (a) β-carotene (b) β-cryptoxanthin and (c) β-carotene + β-cryptoxanthin. The straight lines describe how the data fit the first-order reactions at each temperature: 100 °C (square), 110 °C (diamond), 130 °C (triangle), 140 °C (circle) and 150 °C (cross).

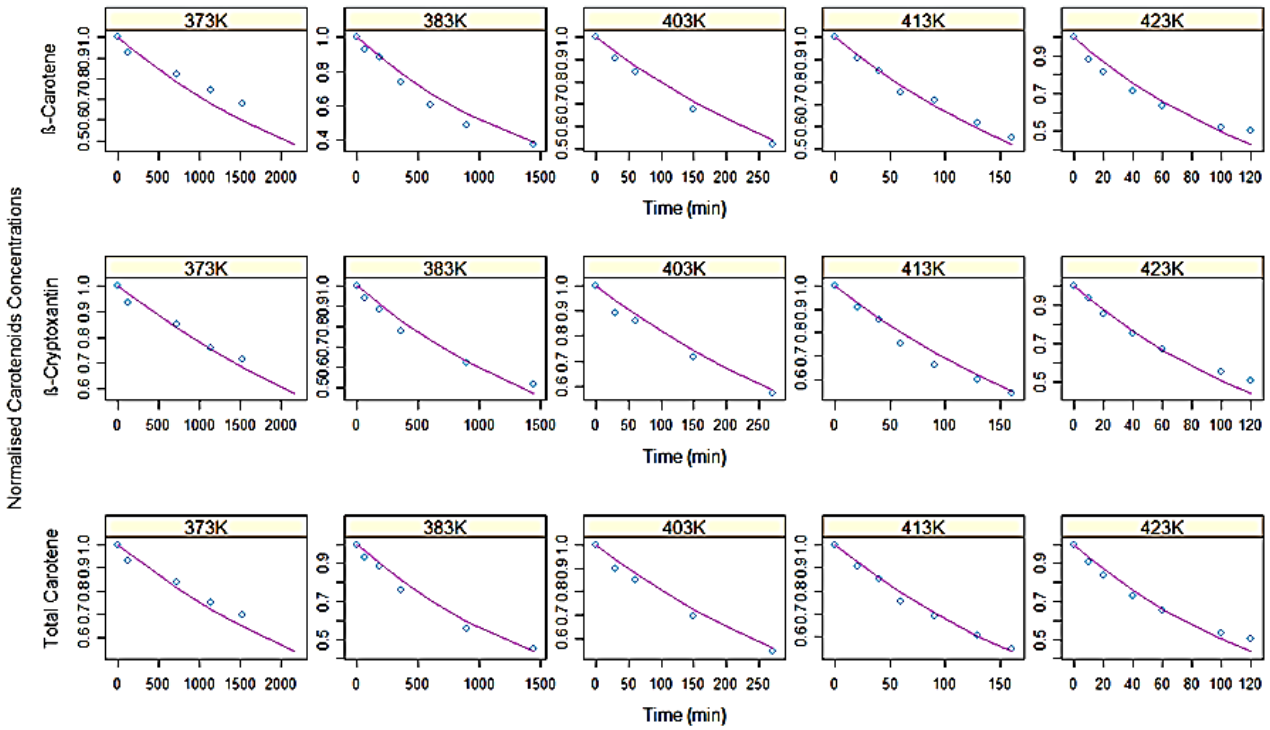

Figure 5.3.2.2. Relative concentrations of β-carotene, β-cryptoxanthin, overall carotenoids (β-carotene + β-cryptoxanthin), after the thermal treatments of macauba mesocarp oil, modelled by one-step regression. The single data points represent the experimental values, whereas the full lines represent the values predicted by the kinetic model.

It can be observed that the results between 373.15 K and 423.15 K indicated that the first-order kinetic model is appropriate for describing the oxidative degradation of β-carotene, β-cryptoxanthin and overall carotenoids (β-carotene + β-cryptoxanthin) in the macauba oil. The model fits the experimental data fairly well (Lemmens et al., 2011). The dimensionless concentrations for all the treatments decreased as a function of heating time becoming faster at higher temperatures and visible macroscopically by a loss of colour. It was determined a definite influence of temperature on the oxidant reactions rates of β-carotene and β-cryptoxanthin, based on the Arrhenius model. The findings agree with observations by Knockaert et al. (2012), Fratianni et al. (2010) and Henry et al. (1998).

The intensity of the thermal treatment is an important factor to be controlled being related to the impact of temperature increase on carotenoid retentions in the macauba mesocarp oil. As an essential unity operation, the thermal processing likewise influences both carotenoids bioaccessibility (Lemmens et al., 2011; Palmero et al., 2013) and the health-related attributes of vegetable oils (Rodriguez-Amaya et al., 2006; Nunes et al., 2015; Hiane et al., 2005; Magosso et al., 2016).

As previously discussed, the initial state of the oil may have contributed to carotenoid oxidation (Achir et al., 2010). The predominance of unsaturated fatty acids in the oil might also collaborate to enhancing oxidative reactions which already took place even at the lower temperature of 373.15 K but became more pronounced as the temperature increased. The corresponding initial degradation rates r (min^{-1}) were found to increase with temperature from 6.1 x 10^{-4} min^{-1} (at 100 °C) to 93.5 x 10^{-4} min^{-1} (at 150 °C) for β-carotene, and from 5.5 x 10^{-4} min^{-1} (at 100 °C) to 72.0 x 10^{-4} min^{-1} (at 150 °C) for β-cryptoxanthin. Therefore, the rates were similar for both compounds. In the 100–150 °C temperature range, the initial degradation rates increased by around 15-fold for β-carotene and by around 13-fold β-cryptoxanthin. The similarity of the temperature sensitivity increase for the two compounds was confirmed by the kinetic data derived from these experiments.

Table 5.3.2.1 lists the estimated reaction rate constant at the reference temperature of 403.15 K (k_{ref}), the activation energy (E_a), the adjusted regression coefficient (R^2_{adj}) and the residual standard error (RSE). It is noted that model parameters are apparent, which is typical when data are expressed on food systems with reactions occurring in a certain phase (Colle et al., 2013).

Table 5.3.2.1. Kinetic Parameters ± Standard Deviation (based on 95% confidence interval) estimated by one-step regression analysis for the carotenoids degradation due to Thermal Treatments of Macauba Mesocarp Oil.

Reactions	Kinetic Parameters				
	E_a (kJ.mol^{-1})	k_{ref} (x 10^{-3} min^{-1})	Ln (A)	R^2_{adj}	RSE[c]
Individual β-carotene	80 ± 3	1.2 ± 0.1	17.7 ± 1.0	0.95	0.04
Individual β-cryptoxanhin	87 ± 3	1.0 ± 0.0	19.7 ± 1.0	0.97	0.03
Overall carotenoids[a]	84 ± 3	1.1 ± 0.1	18.9 ± 1.0	0.97	0.03
SD-TC[b]	80 ± 3	0.9 ± 0.1	17.5 ± 1.0	0.96	0.03

[a] β-carotene + β-cryptoxanthin.
[b] Spectrophotometric Determination of Total Carotenoid, as described in Section 5.2.4.
[c] Residual Standard Error.

When the kinetic parameters are compared from Table 5.3.2.1., it can be seen that the rate constants are similar for the studied compounds being slightly higher for β-carotene compared to β-cryptoxanthin, as well as to overall carotenoids (β-carotene + β-cryptoxanthin). The parameters obtained based on the spectrophotometric determination (SD-TC) are also presented for total carotenoid with the aim of fulfilling comparative purposes. In this sense, the 90% Joint Confidence Regions (JCR) is illustrated in Figure 5.3.2.3 for statistically comparing the

simultaneously estimated parameters E_a and k_{ref} in the oil (Knockaert et al., 2012; Colle et al., 2013). The symbols represent the least-squares estimates; elliptical geometries represent JCRs.

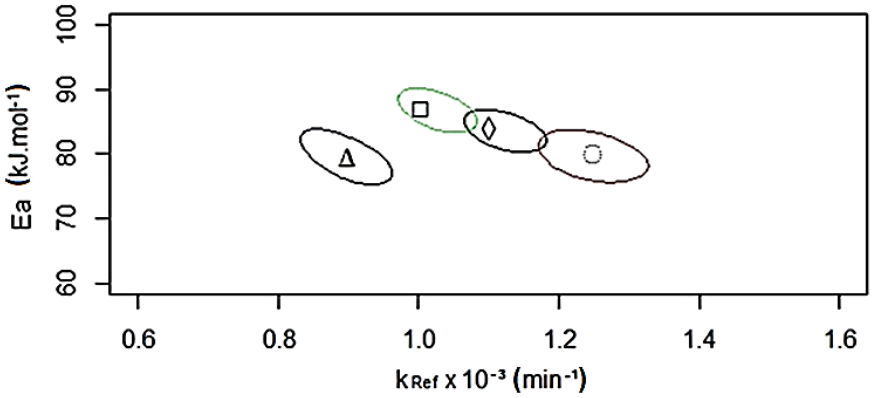

Figure 5.3.2.3. Joint confidence regions (90%) for the carotenoid degradations in macauba oil: β-carotene (○), β-cryptoxanthin (□), overall carotenoids (β-carotene + β-cryptoxanthin) (◊) and SD-TC (total carotenoid content determined by spectrophotometric method) (Δ).

For β-carotene and β-cryptoxanthin degradations, JCR does not overlay which indicates that the correlated combinations of k_{ref} and E_a for the two compounds are significantly different from one another, in macauba oil, at a confidence level of 90%. It can be stated that β-carotene is more labile under the described conditions and degraded more rapidly compared to β-cryptoxanthin. The higher apparent activation energy observed for β-cryptoxanthin as compared to β-carotene implies that a smaller temperature change is needed to degrade β-cryptoxanthin more rapidly. Although there is still a lack of kinetic data in macauba oil, the results are similar to those observed by Dhuique-Mayer et al. (2007) and might be attributed to the compound type, chemical structure and reactivity toward radicals.

Consistent with our study, Achir et al. (2010) reported the apparent activation energy of 86 ± 9 kJ.mol^{-1} for the degradation of *trans*-β-carotene in palm olein. On the other hand, a broad range of activation energies have been reported in the literature (Knockaert et al., 2012; Aparicio-Ruiz et al., 2011; Sampaio et al., 2013; Dhuique-Mayer et al., 2007; Minguez-Mosquera and Jaren-Galan, 1995) for the degradations of β-carotene (45-110 kJ.mol^{-1}) and β-cryptoxanthin (67-156 kJ.mol^{-1}). Even though agreements are observed for estimated kinetic parameters, variations between studies may derive from different ranges of temperatures applied being highly dependent on the reaction medium (Colle et al., 2013; Henry et al., 1998).

The combination of k_{ref} and E_a determined for the sum of β-carotene + β-cryptoxanthin is not significantly different from those determined for each of the individual compounds as the JCR for overall carotenoids is overlapped once by β-carotene and again by β-cryptoxanthin. In this sense, a brief discussion arises from the application of kinetic parameters estimated for overall carotenoids to predict the retention of individual compounds with relative accuracy in the context of industrial scale processes. Herein, a tendency of linear correlation between the kinetic parameters $E_{a\ and}\ k_{ref}$ determined for β-carotene, β-cryptoxanthin, and overall carotenoids may be possibly observed. To some extent, it reinforces the possibility to examine if the studied reactions could potentially proceed through similar mechanisms in the macauba mesocarp oil, as discussed later in section 5.3.3 (Krug et al., 1976a).

In the context of enlarging possibilities for processes design on nutraceutical products, the analytical determination of carotenoids is also a decisive step on kinetic modelling. In this sense, Figure 5.3.2.3 allows observing that the combinations of k_{ref} and E_a estimated for total carotenoids based on the spectrophotometric determination (SD-TC) are qualitatively and quantitatively different from those estimated based on chromatography. Even though similarities can be noted between apparent activation energies, differences are definite for the parameter rate constant at the reference temperature of 403.15 K (k_{Ref}), being lower for SD-TC then for β-carotene, β-cryptoxanthin and overall carotenoids. Indeed, the accuracy of spectrophotometric methods tend to be usually suitable for screening purposes as it is not as high as of HPLC (Rodriguez-Amaya and Kimura 2004). These findings reinforce that accurate quantitative measurements of carotenoids must fit the analytical purpose being imperative for probing its function.

5.3.3 Thermodynamic Considerations

The results obtained from transition state theory and the correspondent correlation coefficients are displayed in Table 5.3.3.1 for the β-Carotene and β-cryptoxanthin degradation reactions. In all cases, $T\Delta S^{\#}$ values were always negative. However, enthalpy of activation values ($T\Delta S^{\#}$) were always positive, as were the Gibbs free energy values (ΔG). Under the experimental conditions, the results indicate that the formation of the activated complex for carotenoids occurs non-spontaneously. In summary, the increase in the energy or enthalpy of activation often does not provoke an expected decrease in the rate constant of the reaction since there is usually a simultaneous increase in the frequency factor or entropy of activation. These findings adhere to the kinetic modelling performed in the present study as it considers the close correlation between k_0 and E_a.

Table 5.3.3.1. Overview of the thermodynamic parameters: Degradation reactions of β-carotene and β-cryptoxanthin.

Reaction	$\Delta H^{\#} \pm SD^{b}$ (kJ.mol^{-1})	$\Delta S^{\#} \pm SD^{b}$ (kJ.mol^{-1} K^{-1})	$\Delta G \pm SD^{b}$ (kJ.mol^{-1})	R^2
β-carotene	77.62 ± 6.30	-0.14 ± 0,01	134.24 ± 8.75	0.98
β-cryptoxanhin	85.84 ± 3.51	-0.12 ± 0.01	134.63 ± 3.46	0.99
Overall carotenoids[a]	81.47 ± 4.22	-0.13 ± 0.01	134.43 ± 9,42	0.99

[a] β-carotene + β-cryptoxanthin.
[b] Standard Deviation

As it can be seen in Figure 5.3.3.1a, plotting the enthalpies of activation ($\Delta H^{\#}$) *versus* entropies of activation ($\Delta S^{\#}$), yield a compensation plot, typically a straight line (Rudra et al., 2008; Henry et al., 1998). It can be observed in Figure 5.3.3.1b that plotting the logarithm of the pre-exponential factors Ln(*A*) *versus* activation energies also yields a straight line (Collet and Rand, 1980; Liu and Guo, 2001).

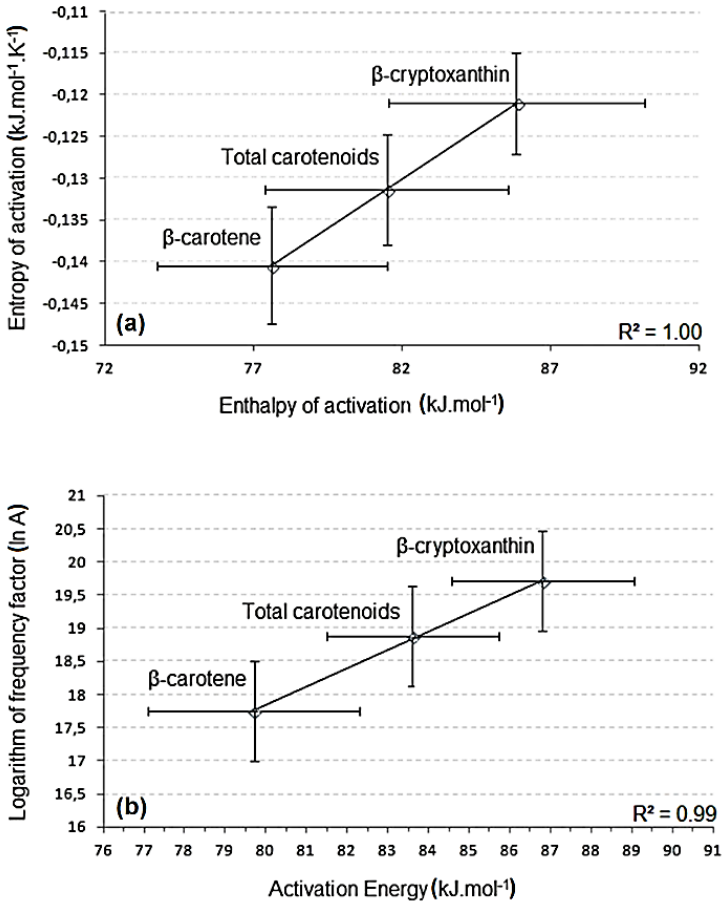

Figure 5.3.3.1. Regression lines for carotenoids degradation reactions: (a) Enthalpy of activation *versus* entropy of activation, with 5% error bars; (b) Apparent activation energy *versus* logarithm of frequency factor, with standard error bars.

The enthalpy-entropy compensation is widely debated as a potential phenomenon in chemical processes. Some studies suggest that the compensation effect is true when there is a linear correlation between the enthalpies and entropies of activation or between the logarithm of the pre-exponential factors and the activation energies of similar reactions. The phenomenon, particularly, refers to the idea that variations in enthalpy that accompany variations in temperature during chemical reactions are compensated for by changes in entropy (Collet and Rand, 1980; Labuza, 1980; Minguez-Mosquera and Jaren-Galan, 1995; Henry et al., 1998).

It is observed that even though the estimated ΔG is approximately constant the parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ vary within the reactions series. According to Exner (1964), this type of behaviour is an indicator of the compensation effect. It should be, however, stressed that the mentioned phenomenon is sometimes based on the assumption that the data used in the correlation are error free. Considering that errors of experimental measurements are unavoidable, it may be suggested that the correlation data could be estimators of the corresponding parameters (Liu and Guo, 2001; Rudra et al., 2008; Collet and Rand 1980). As a matter of fact, Petersen et al. (1962) stated that if the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) are measured for a series of reactions using the same temperatures throughout the series, the experimental error in $\Delta S^{\#}$ tends to be directly proportional to the experimental error in $\Delta H^{\#}$. Therefore, if the range of values of the parameters is not as extensive as that of the experimental error, the straight line of the slope may be a demonstration of the experimental error.

In summary, the present observation of a correlation between either the experimental $\Delta H^{\#}$ and $\Delta S^{\#}$ or $\ln(A)$ and E_a cannot, by itself, be taken as evidence for the existence of the compensation effect. On the other hand, explicitly drawing the error bars (or confidence region) in the correlation diagram may potentially indicate the existence of the effect. In this regard, the linear dependencies observed in Figure 5a and Figure 5b could, to some extent, be related to the assumption that the thermal degradation of carotenoids in the macauba mesocarp oil may proceed through similar mechanisms (Henry et al., 1998; Labuza, 1980; Minguez-Mosquera and Jaren-Galan, 1995). However, this should not be concluded only by the linearity of the enthalpy and entropy graphs. As the compensation effect is an empirical relationship, critical judgment by statistical analysis would be recommended to test for the propagation of errors and its resulting effect on the linearity (Collet and Rand, 1980; Rudra et al., 2008; Exner, 1964). An itemised analysis of this phenomenon is discussed by Krug et al. (1976b,c) and Liu and Guo (2001) and requires further investigation.

5.4 Conclusions

This study has developed the kinetic modelling involving the thermal degradation of natural carotenoids in the macauba mesocarp oil. The first-order kinetic model was appropriate for describing the oxidative degradation of β-carotene and β-cryptoxanthin in the edible oil. The overall disappearances of the compounds were strongly activated by temperature. On the one hand, β-carotene was shown to be more labile than β-cryptoxanthin under the studied conditions. On the other hand, a higher apparent activation energy was observed for β-cryptoxanthin as compared to β-carotene, which implies that smaller temperature changes are needed to degrade β-cryptoxanthin more rapidly. The correlated combination of k_{ref} and E_a determined for the sum of β-carotene + β-cryptoxanthin indicated that the parameters estimated for overall carotenoids might predict the retention of the individual compounds with relative accuracy in the context of industrial scale processes. Results obtained from transition state theory to some extent may be related to the assumption that the thermal degradation of carotenoids could proceed through similar mechanisms in the macauba mesocarp oil. Overall, the results open up perspectives for new processes development and inspire the use of kinetic data and procedures that aim to understand the thermal processing of the macauba oil as an alternative and functional raw material for industrial applications.

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Practical applications

This paper contributes an assessment of the stability of carotenoids of macauba oil. Kinetic models to predict the effect of processing on carotenoids are proposed, which will help food processing research to define appropriate ways to process macauba oil without affecting these bioactives.

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CHAPTER 6. Kinetic Predictions of Total Carotenoids Retention in Macauba Oil Under Interesterification Conditions

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Abstract

Recently, the world consumption of palm oils has increased significantly. Under the perspective of industrial applications, several processes are conducted to modify native vegetable oils to meet functional performances of structured lipids. In this sense, the recent scientific and technological advances related to interesterification open up perspectives for new products and processes developments. Macauba oils are, thus, presented as alternative raw materials for industrial purposes that might also include interesterification. This study was undertaken with the primary objective of considering conventional processing conditions applied for the interesterification of vegetable oils to kinetically predicting the thermal effects on the retention of natural carotenoids in the *Acrocomia aculeata* oil. The kinetic predictions carried out in this study considered data given by previous studies making it feasible to evaluate possible thermal effects on the retention of carotenoids naturally present in the oil studied. The benefiting obtained from the potential retaining of bio-compounds in the macauba feedstock for producing structured lipids with special appeals is highlighted. The computational capabilities inspiring the use of kinetic data and procedures aiming knowledge and understanding of thermal food processing is also pointed out.

Keywords: carotenoids, kinetics, interesterification

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6.1 Introduction

The world consumption of vegetable oils increased significantly in recent years (USDA, 2016; Graham-Rowe, 2011; Da Silva, 2013). Along the period between 2008 and 2017, this consumption has also been driven by food production to represent a growth of around 43%, reaching 183 million metric tonnes. The world consumption of palm oils followed the mentioned increased to represent 35% of the global volume registered in 2017 (USDA, 2017).

Under the perspective of industrial applications, several processes are proposed to modify native vegetable oils. These modifications are usually conducted to meet functional performances of structured lipids, including plasticity, tractility and shortening property (Xie et al., 2015; Xu, 2000). Among the most commonly applied methods to tailor physicochemical properties of edible oils, interesterification has received much attention. Unlike hydrogenation, interesterification processes are not related to the formation of *trans* fatty acids in final products. Therefore, interesterification methods potentially extend the commercial application of modified lipids to the production of a wide variety of foodstuffs, including functionals (Gibon, 2011).

It becomes relevant to highlight that interesterification process of vegetable oils are usually carried out chemically or enzymatically. Both reactions promote rearranges in the distribution of the fatty acids located in the triacylglycerol structures, preserving the fatty acids profiles. The process consists of simultaneous ester breakages with the formation of new aleatory bonds (Costales-Rodriguez, 2009).

It is emphasised that chemical interesterification has been a widely applicable process in which low-acid vegetable oils are not required to be previously bleached. Being inexpensive when compared to enzymatic interesterification, the method is amenable to be scaled up and also considered efficient, relevant and feasible in the edible oil industry (Osborn and Akon, 2002; Scrimgeour and Harwood, 2007).

Under the perspective of industrial processes, chemical interesterification tends to be carried out considering homogeneous base catalysts, typically sodium methanolate $NaOCH_3$ (Dijkstra, 2015; Marangoni and Rousseau, 1995; Rodriguez et al., 2001). Although these catalysts are robust and low-cost, the need for their inactivation and removal at the end of each process is required. Thus, attention is deserved regarding possible contaminations of structured food lipids (Soares et al., 2012). Consequently, besides reducing oil yield, the necessity of eventual post-treatments steps (*i.e.* bleaching, deodorisation) can contribute to increasing processes costings also removing valuable micronutrients naturally present in various native vegetable oils (Dijkstra, 2015).

In this framework, heterogeneous catalysts have received recent attention as a way of overcoming drawbacks related to homogeneous interesterification. These catalysts contribute with several industrial advantages which include high catalytic activity, easiness of separation and recyclability. In this sense, heterogeneous interesterification is shown to apply to reduce post-treatments steps also enabling the retention of bio-compounds in final structured lipids. By consequence, the method apparently opens up perspectives for new processes development also related to special food productions. Indeed, the potential of the method to meet food specifications has already been shown (Dijkstra, 2015; Xie and Xen, 2014; Xie and Qi, 2013).

It is certain that successful synergies to be reached in the current scenario may require a continuous focus on contextual problems and opportunities. In this sense, it is highlighted the increasing demand recently shown by consumers and industries with regard to natural food and products (Cataldo et al., 2016; Babbar et al., 2015; Gonçalves et al., 2014). Noticeably, that the consumption of these products tends to be associated with the health-related benefits obtained from bioactive compounds, among which fatty acids, carotenoids and micronutrients constitute important classes (Juárez-Hernández et al., 2016; Babbar et al., 2015; Lim and Kim, 2016).

In this scenario, macauba (*Acrocomia* aculeata) is presented as an alternative crop for purposes that also include interesterification processes. Macauba is one of the most widespread palms in the Neotropics (Uhl and Dransfield, 1987; Scariot et al., 1995). With a similar productive potential to *Elaeis guineensis* (FAO, 2013; Evaristo et al., 2016) this high oil-yielding plant is suited to edaphoclimatic zones, which feature conditions averse to African palms (Lanes et al., 2016).

An adult macauba palm fructifies almost the whole year with productivity from 4 to 6 tonnes of esculent oil per hectare. Regarding the oil extracted from the mesocarp, it is readily edible and contains up to 378 $mg.kg^{-1}$ of carotenoids. The esculent oil has a predominance of unsaturated fatty acids (77%) of which 53% and 18% are oleic (ω-9) and linoleic (ω-6), respectively. The edible oil extracted from the kernel has a predominance of saturated fatty acids (74%), of which 44% and 9% are lauric and palmitic, respectively (Nunes et al., 2012; Rettore and Martins, 1983).

Remarkably, the macauba fruit provides two different types of edible oils which can be suggested to be together used as raw materials for the production of structured lipids. In fact, industrial efforts have already become remarkable and can be verified in the sense of producing different blends of vegetable oils to enhance the nutritional characteristics of structured and interesterified lipids with specific functional properties (Grimaldi et al., 2005; Norizzah et al., 2004; Rodriguez et al., 2001; Petrauskaite et al., 1998; Lida and Ali, 1997).

From the perspective of lipid processing and structuring, it is of importance to point out that thermal treatments become essential unity operations to be controlled concerning the retention of several bioactive compounds in vegetable oils. Especially on carotenoids, the incidence of temperature has indeed been proven to likewise influence both compounds bioaccessibility (Lemmens et al., 2011; Palmero et al., 2013) and the health-related attributes of vegetable oils (Rodriguez-Amaya et al., 2006; Nunes et al., 2015; Hiane et al., 2005; Magosso et al., 2016). Indeed, the rates of the degradation reactions tend to dramatically increase during thermal treatments, as a function of heating time, varying as temperature rises (Knockaert et al., 2012; Dellamonica and Mcdowell, 1965; Achir et al., 2010; Sampaio et al., 2013).

In this scenario, it is highlighted that mathematical and predictive modelling through experimental and computer simulation techniques have benefiting from new computational capabilities that inspiring the use of kinetic data and procedures that aim knowledge and understanding of thermal food processing (Singh et al., 2015). Thus, the present study was undertaken with the primary objective of kinetically predicting the retention of natural carotenoids in the macauba mesocarp oil by considering the thermal effects of conventional processes conditions usually applied for the interesterification of vegetable oils.

6.2 Procedures

6.2.1 Fruit pre-processing

Macauba fruit was collected from native palms with a maximum of five days after the fall in the area of the Universidade Federal de Minas Gerais, in the metropolitan region of Belo Horizonte, Minas Gerais, Brazil. The macauba mesocarp and kernel were promptly separated from the fruit. Before the oil extraction, these parts were thawed, air dried at 60 °C for 48 hours and comminuted in an electric grinder coupled to a stainless steel cup (Pimenta, 2010; Goula, 2013). The mesocarp and kernel pressings were performed on different days, avoiding any cross-contamination

6.2.2 Oil processing

The samples consisted of edible oils mechanically obtained from the mesocarp and kernel of fresh macauba fruit by continuously operated *Expeller*® press. 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 until the analysis (Koidis and Boskou, 2014; Parducci and Fennema, 1978).

6.2.3 Determination of Fatty Acid Compositions

Based on the methods previously optimised by Christie (1989) and Guo et al. (2011), the fatty acids compositions were determined for the edible macauba mesocarp and kernel oils. The analysis was carried out on a GC- 2010 System (Shimadzu, Japan) fitted with a Flame Ionisation Detector. Quantification of individual fatty acids methyl esters – FAME was conducted with a standard mixture of 37 esters of fatty acids (Supelco, Bellefonte, Pa., USA).

6.2.4 Determination of Acid Value

The Acid Value (AV) for the macauba mesocarp oil was determined according to the AOCS Official Method 3d Cd-63 (AOCS, 2009).

The determinations were performed by diluting 1 g of oil in 50 mL solution of isopropanol:toluene (1:1) followed by titration with potassium hydroxide (0.1 $mol.L^{-1}$) standardised with potassium biphthalate. The AV were calculated by the equations (1) and (2).

$$AV\ (mg\ KOH.g-1) = \frac{(A-B)\ \text{x}\ M\ \text{x}\ 56.1}{W} \quad (1)$$

$$AV\ (\%\ oleic\ acid) = \frac{(A-B)\ \text{x}\ M\ \text{x}\ 28.2}{W} \quad (2)$$

Where,

A = KOH volume (mL) used for the sample titration
B = KOH volume (mL) used for the blank titration
M = Molarity of the base, after standardisation
W = Weight (g) of the sample

6.2.5 Spectrophotometric Determination: Total Carotenoids

The spectrophotometric determination of the initial concentration of total carotenoids occurred using a Hach DR 2800 spectrophotometer (Hach, Loveland, CO, USA) as recommended by Rodriguez-Amaya and Kimura (2004) and suggested by PORIM (1990).

The quantification ($mg.kg^{-1}$) considered an absorption coefficient (A1%1cm) of 2580 in high purity n-hexane (Zscheile et al., 1942).

6.2.6 Kinetic Prediction: Total Carotenoids retention

In order to predict the retention of total carotenoid in the macauba mesocarp oil, the processing parameters related to the interesterification were defined based on Grimaldi et al., (2005), Norizzah et al. (2004), Rodriguez et al. (2001), Petrauskaite et al. (1998) and Lida and Ali (1997). The isothermal temperature (Dinh et al., 2016) of 393.15 K was considered along the processing time of 120 minutes.

The prediction of the carotenoids retention was carried out using MS Excel software, version 16.0.6001.1070 (Washington, USA). The different kinetic parameters used to evaluate the maintenance of total carotenoids in the macauba oil are given by Achir et al. (2010), Henry et al., (1998), Aparicio-Ruiz and Mínguez-Mosquera (2011) and Knockaert et al. (2012) and compared considering the presented processing parameters.

The first-order kinetic model was considered appropriate for predicting the total carotenoids retention in macauba vegetable oils. The lack of data related to the thermal degradation of carotenoids in macauba oils is noted.

The kinetic predictions considered data obtained from the following equation (3) being expressed relative to the initial concentration of carotenoids as a function of time:

$$P_{carotenoids} = exp\left(-k_{ref}\, exp^{\left(\frac{-E_a}{R}\left(\frac{1}{T_p}-\frac{1}{T_r}\right)\right)_{time}}\right) \quad (3)$$

Where,

T_{ref} = Absolute Processing Temperature (K)

k_{ref} = Specific Rate Constant given by literature

E_a = Activation Energy (J.mol^{-1})

R = Gas Constant (8.314 J.mol^{-1} K^{-1})

Pcarot = Prediction as a function of time

The rate constant (k, min^{-1}) was assumed to vary with the absolute temperature T (K) according to Arrhenius law (Fogler, 2016). In this sense, the reparametrized equation (4) was considered to estimate the rate constant (k) at the defined processing temperature.

$$k = k_{ref}\, exp^{\left(\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)} \quad (4)$$

Where,

T_{ref} = Absolute Reference Temperature (K)

k_{ref} = Rate Constant at the Reference Temperature

k = Specific Rate Constant

E_a = Activation Energy ($J.mol^{-1}$)

R = Gas Constant (8.314 $J.mol^{-1}$ K^{-1})

As a definition, it is worth noting that the equation (5) is given for the study of carotenoids changes:

$$\frac{dC}{dt} = -kC^n \quad (5)$$

The presented equation (4) conveys that the degradation rate dC/dt is proportional to the nth power of carotenoids concentration (C in $mg.kg^{-1}$ of oil) at any time t, while n is the order of the reaction and k (1/time) is the reaction constant.

6.3 Results

6.3.1 Results for the Fatty Acid Composition

Table 6.3.1.1 shows the mean and standard deviation for the fatty acid composition (expressed as a percentage of total fatty acids) for the oils extracted from the macauba mesocarp and kernel. It can be observed the predominance of oleic acid in the mesocarp oil. Relevantly, the level is similar to those (48-74%) of palm stearin (CAC, 2015), which is widely used for interesterification purposes.

The palmitic acid was the second most abundant fatty acid in the oil extracted from the macauba mesocarp, which is in agreement with previous reports (Hiane et al., 2005; Nunes et al., 2015; Rettore and Martins, 1983). Lauric acid was the predominant fatty acid in macauba kernel, what also occurs to other palm crops such as babassu and the kernel oil, kernel olein and kernel stearin of *Elaeis guineensis* (CAC, 2015).

The predominance of unsaturated fatty acids (MUFA: 62.11 ± 0.84%; PUFA: 11.37 ± 1.23%) was observed for the mesocarp oil. On the other hand, the predominance of saturated fatty acids became apparent for the kernel oil (SFA: 63.75 ± 0.84%).

Regarding the ω-6 family of fatty acids, the linoleic acid in the macauba mesocarp (8.81%) and kernel (3.94%) oils were similar to those reported (CAC, 2015) for palm oil (9.0-10.0%), palm stearin (3.0-10.0%), sunflower oil (2.1-17.0%) and virgin and refined olive oils (3.5-21.0%). The contents of linoleic acid in the macauba oils were, yet, higher than those registered for palm kernel oil (1.0-3.5%), palm kernel olein (2.4-4.3%) and palm kernel stearin (0.5-1.5%).

Table 6.3.1.1. Fatty acid compositions, expressed as percentage of total fatty acids

Fatty Acid	**Macauba Palm (*Acrocomia aculeata*)**	
	Mesocarp Oil	**Kernel Oil**
Caproic acid (C6:0)	ND[b]	0.35 ± 0.00
Caprylic acid (C8:0)	0.08 ± 0.05	4.38 ± 0.04
Capric acid (C10:0)	ND[b]	3.62 ± 0.03
Undecylic acid (C11:0)	0.08 ± 0.04	ND[b]
Lauric acid (C12:0)	0.04 ± 0.01	37.22 ± 0.03
Myristic acid (C14:0)	0.07 ± 0.00	8.12 ± 0.02
Pentadecylic acid (C15:0)	0.17 ± 0.00	0.03 ± 0.00
Palmitic acid (C16:0)	19.62 ± 0.56	6.88 ± 0.02
Palmitoleic acid (C16:1)	1.68 ± 0.04	0.16 ± 0.01
Margaric acid (C17:0)	0.09 ±0.00	0.04 ± 0.00
Ginkgolic acid (C17:1)	0.06 ± 0.00	0.04 ± 0.00
Stearic acid (C18:0)	5.15 ± 0.17	2.90 ± 0.02
Oleic acid (C18:1)	60.33 ± 1.18	32.0 ± 0.01
Linoleic acid (C18:2)	8.81 ± 0.32	3.94 ± 0.02
α-Linolênic acid (C18:3)	0.73 ± 0.02	0.06 ± 0.00
Arachidic acid (C20:0)	0.21 ± 0.00	0.14 ± 0.00
Gadoleic acid (C20:1)	0.07 ± 0.01	0.14 ± 0.01
Behenic acid (C22:0)	0.14 ± 0.01	0.09 ± 0.01
Eicosadienoic acid (C20:2)	1.83 ± 0.46	ND[b]
∑ SFA[a]	25.65 ± 0.84	63.75
∑ MUFA[b]	62.14 ± 1.23	32.32
∑ PUFA[c]	11.37 ± 0.80	3.93

[a]Saturated Fatty Acids, [b]Monounsaturated fatty acids, [c]Polyunsaturated fatty acids
[b]*ND - Non-detectable, defined as ≤ 0.05%*

The clear distinction between the fatty acid profiles of macauba mesocarp and kernel oils, especially regarding the contents of saturated and unsaturated fatty acid, already renders it an important role as a potential alternative oil crop for interesterification purposes. Indeed, the fatty acid compositions of these two types of oils are similar to that of other broadly used raw materials mainly blended to meet and improve functional performances of structured lipids (Xie et al., 2015; Xu, 2000).

6.3.2 Results for acid value and total carotenoids

The following Table 6.3.2.1. shows the mean and standard deviation for the Acid Values in the macauba mesocarp oil, also presenting the initial content of total carotenoids determined spectrophotometrically.

Table 6.3.2.1. Acid value and total carotenoids: macauba mesocarp oil

Determinations	Mesocarp Oil
Acid Value (mg KOH.g^{-1})	1.6 ± 0.1
Acid Value (% oleic acid)	0.8 ± 0.1
Total Caroteniod (mg.kg^{-1})	248.0 ± 8.0

As it can be seen, the contents of free fatty acids – FFA were well below the limit of 4.0 mg KOH.g^{-1} established by the Resolution RDC 270, of the Brazilian Health Regulatory Agency – ANVISA (Brasil, 2005), for cold, pressed and non-refined edible vegetable oils. It is highlighted that the acid value has already been widely determined in literature for the macauba kernel oil (Rettore and Martins, 1983; Pimenta, 2010; Coimbra and Jorge, 2011; Hiane et al., 2005). It has been, therefore, observed that the FFA in kernel oils range from 0.3 to 0.7 (mg KOH.g^{-1}) which are usually much lower than that of mesocarp oils. In fact, lipolytic enzymes catalyse the decomposition of triglycerides and tend to be most active in mesocarps (Coimbra and Jorge, 2011).

Above all, low values of acidity observed for the oils extracted from the macauba mesocarp and kernel adheres to interesterification purposes (Osborn and Akon, 2002; Scrimgeour and Harwood, 2007) reinforcing the macauba oils as raw materials for industrial uses.

Regarding total carotenoids in the macauba mesocarp oil (248.0 mg.kg^{-1}) the content surpasses of other tropical fruits becoming one of its remarkable characteristics (Rufino et al., 2010; Rodriguez-Amaya, Kimura and Farfan, 2008). Consistent with our observations, Nunes et al. (2015) and Coimbra and Jorge (2011) reported the crude macauba oil to contain above 300 mg.kg^{-1} of total natural carotenoids. Wherefore, although some variability in the carotenoid content tends to be noted for different macauba genotypes, it is suggested that, once preserved in final products, these bio-active compounds may enrich the composition of structured lipids derived from macauba oil to compete against products that don't have that natural appeal (Cataldo et al., 2016, Babbar et al., 2015; Gonçalves et al., 2014).

6.3.3 Kinetic Prediction of Carotenoids retention

The kinetic predictions of the thermal effects on the natural carotenoids maintenance in the macauba mesocarp oil are presented in Figure 6.3.3.1. The results are expressed relative to the initial concentration, as a function of time.

It is observed that the extreme conditions (2 h; 393.15 K) similar to those of interesterification appeared to significantly decrease the initial amount of total carotenoids in the macauba mesocarp oil. Notably, the total carotenoids were reduced by at least around 70% and 80% when considering the kinetic parameters (apparent activation energies and rate constant) given by Achir et al. (2010) and Knockaert et al. (2012), respectively.

A further comparison considering all the predictions showed that after 50 minutes at least around 40% of the total carotenoid might have been degraded as a consequence of temperature supply. It leads to verify that around 148 $mg.kg^{-1}$ of carotenoids would remain in the oil extracted from the mesocarp after this processing time. Importantly, as expected, the dimensionless concentrations of carotenoids always decreased as a function of heating time, independently of the kinetic data used for the prediction.

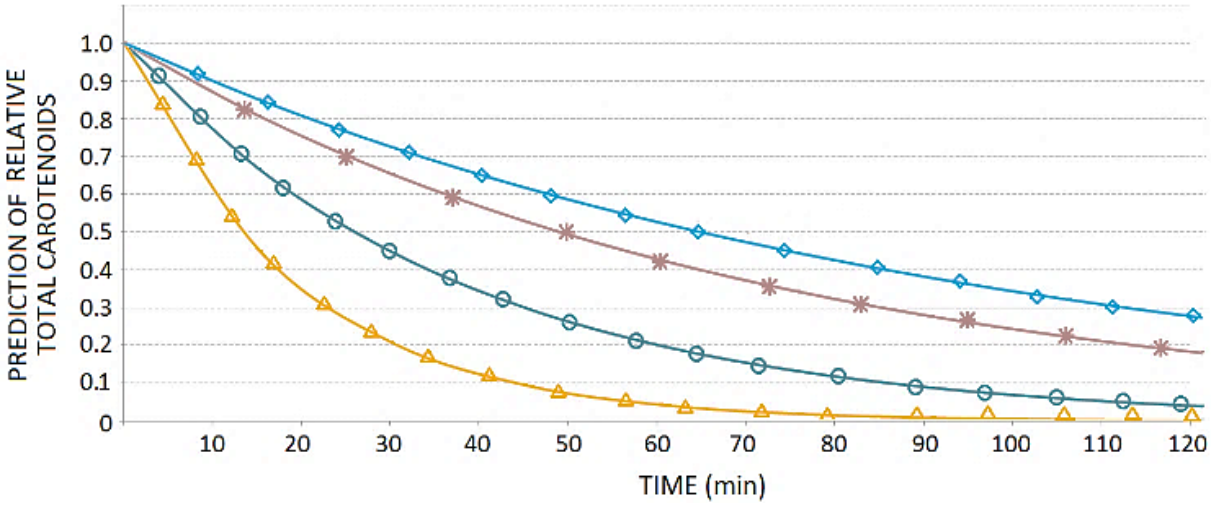

Figure 6.3.3.1. Prediction of thermal effects on the retention of natural carotenoids in the macauba mesocarp oil, expressed relative to the initial concentration as a function of time: Achir et al. (2010) – filled diamond, Henry et al.(1998) – filled triangle, Aparicio-Ruiz and Mínguez-Mosquera 2011) – filled circle and Knockaert et al. (2012) – filled star.

Indeed, from the perspective of industrial thermal processing, the highly unsaturated structures of carotenoids does make the compounds considerably sensitive to thermal degradation reactions (FAO, 1995, Achir et al., 2010). Moreover, rates of the carotenoids degradation reactions have been reported to dramatically increase during different thermal treatments varying with increases of temperature (Achir et al., 2011; Dellamonica and Mcdowell, 1965). It is, therefore, noted that the temperature intensity is an important factor to be controlled along the processes regarding total carotenoid retentions in macauba oil

It can also be observed (Fig. 6.3.3.1.) a significant variability between the predictions. In fact, if the data given by previous studies is carefully analysed, it is possible to verify quantitative differences in the kinetic data provided by different authors. This comparison may indicate that carotenoids degradation appears to be complex and highly dependent on factors linked to the food systems and the matrix they are studied. In this sense, it is stated that studies considering the thermal degradation kinetics of carotenoids in macauba oil are imperative for obtaining data even more reliable for future contributions.

Particularly in engineering, kinetic data also is used for designing products, efficient processes and large-scale reactors. Thus, studies that aim knowledge and understanding on the thermal degradation of bioactive compounds, such as naturally present carotenoids in macauba oils, may adequately probe its kinetic function. As a possibility, the use of specific kinetic parameters may, indeed, not only predict the retaining of high levels of bioactive compounds but access the compliance of specific products to legal standards (Sampaio et al., 2013; Nunes et al., 2015).

6.4 Conclusions

This study reinforces the macauba mesocarp and kernel oils as alternative raw materials for industrial purposes, including interesterification. The oils are noteworthily presented with functional properties (e.g. fatty acid profiles) of a similar nature to those of products derived from African palm (*Elaeis guineensis*). The possible joint use of the distinct oils obtained from macauba fresh fruit agrees with the existing efforts for producing different blends of vegetable oils to enhance the nutritional characteristics of structured lipids with specific functional properties. Once recent scientific and technological improvements related to interesterification processes open up perspectives for new products and processes developments, the study considers the retaining of bio-compounds in vegetable oils, particularly carotenoids naturally present in the macauba mesocarp oil, to strengthen *Acrocomia aculeata* oils as alternative feedstock for

industrial purposes, including for producing structured lipids with natural and special appeals. In this sense, the kinetic predictions carried out made it feasible to evaluate possible thermal effects on the retention of natural carotenoids in the macauba mesocarp oil. Taking into account the dependence of carotenoids degradation on factors linked to the food system in which the compounds are contained, the results suggest that specific knowledge on the estimation of kinetic parameters in macauba oils are imperative for obtaining data even more reliable for future contributions. In fact, the study points out computational capabilities in the sense of inspiring the use of kinetic data and procedures aiming accurate knowledge and understanding of thermal food processing. Besides, the research brings up purposes of continuously building knowledge to sustain the *Acrocomia aculeata* productive chain.

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CHAPTER 7. General Conclusions

This chapter provides the key findings of this study.

Given the increasing interest in *Acrocomia aculeata* palm, the understanding of the crop potential for producing edible vegetal oils does open up perspectives for its use as alternative feedstock for multiple purposes, including food processing. In this sense, the comprehensive build up of knowledge carried out in this research is presented beyond a critical factor. It not only aims to continuously sustain the macauba productive chain but also for inspiring further investments in research to explore the high potential of *A. aculeata* products.

• In this framework, *Chapter 1 and 2* considered elements and topics of relevance to the following construction of this doctoral thesis, also presenting a background with respect to the growing scientific and socioeconomic interest in *Acrocomia aculeata.* Adding to the context, Chapter 3 developed a literature review paper introducing the nutraceutical potential of macauba oils as alternative raw materials for food intents. The study drew attention to the natural content of carotenoids in the oil extracted from fresh fruit mesocarps. The highly unsaturated structures of carotenoids were shown to be responsible for the functional properties of such molecules, at the same time, creating challenges concerning the preventing of thermal oxidation and isomerisation. The study brought up the motivation to following purposes of comprehensive characterisation and thermal degradation kinetic experiments, to gain further insight into bioactives in the oil.

• *Chapter 4* has contributed with the first report on the assessment of different extractions conditions to mechanically obtain high-quality *A. aculeata* oil for multi-purpose employments, including food processing. The harvest and post-harvest handlings adopted in advance of the processing and pre-processing steps were indicated to be a major factor in avoiding intense hydrolysis reactions of triglycerides in the oil studied. The low acid values observed for the samples support the commercial exploitation feasibility of the fresh macauba fruit. The study considered the raw material to be a significant tradeoff between degradation resistance and nutritional value because of its high MUFA content, mainly oleic acid. A comprehensive characterisation of edible oils has been completed concerning chemical and physical characteristics, as well as quality and identity parameters. A baseline of information concerning the raw material has been developed, reinforcing the novelty of this study. The results contributed to evidence that co-products derived from macauba may likely have a good consumer acceptance competing against those products that don't have that nutraceutical value and natural appeal. It is suggested that the compliance to legal standards must be pursued, to guarantee the sustainability of the *A. aculeata* productive chain, regardless of the intended market for the feedstock.

• *Chapter 5* developed the kinetic modelling involving the thermal degradation of natural carotenoids in the macauba mesocarp oil. The first-order kinetic model was appropriate for describing the oxidative degradation of β-carotene and β-cryptoxanthin in the edible raw material. Temperature strongly activated the overall disappearances of the compounds. The correlated combinations of k_{ref} and E_a were statistically compared for the reactions studied. The results obtained for the sum of β-carotene + β-cryptoxanthin indicated that the estimated parameters for overall carotenoids might predict the retention of the individual compounds with relative accuracy in the context of industrial scale processes. Thermodynamic parameters were additionally considered to complimentary examine the reactions studied. The results obtained from transition state theory to some extent have been related to the assumption that the thermal degradation of carotenoids could proceed through similar mechanisms in the oil. Overall, the results open up perspectives for new processes development strengthening macauba as an alternative feedstock for multiple applications.

• *Chapter 6* reinforced macauba mesocarp and kernel oils as alternative raw materials for foods purposes. The oils were noteworthily presented with functional properties (e.g. fatty acid profiles) of a similar nature to those of products derived from African palm (*Elaeis guineensis*). The fatty acids profiles were also compared with other of vegetable oils broadly used for blending purposes. The possible joint use of the oils distinctly obtained from macauba fresh fruit was presented to agree with the already existing efforts for producing different blends of vegetable oils as a way of enhancing the nutritional characteristics of structural lipids with specific functional properties for the oleochemical industry. Indeed, recent scientific and technological improvements have enlarged possibilities for new products and processes developments. Therefore, the evidence on retention of carotenoids strengthened the role of *Acrocomia aculeata* as an alternative source of feedstock for diverse industrial purposes, including for structuring lipids with natural and functional appeals. In this sense, kinetic predictions were thereby carried out for making it feasible to evaluate possible thermal effects on the carotenoids retention in the oil studied which may result from interesterification processing conditions. The research timely took into account computational capabilities that have either emerged the use of specific kinetic data and procedures to understand thermal processing as an essential unity operation on food context

Overall, the doctoral thesis has assessed the processing effects and conditions, integrating results and knowledge regarding one of the highest oil-yielding plants in the world, improving the prospects of *Acrocomia aculeata* as a promising source of high-quality raw material, for multi-purpose application, including for producing novel food.

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SCOIL EOLAÍOCHT AN BHIA & SLÁINTE AN CHOMHSHAOIL /
SCHOOL OF FOOD SCIENCE & ENVIRONMENTAL HEALTH:

June 29th, 2016

To whom it may concern,

I been in contact with Mr Pedro Prates Valério regarding his application for a stage research period during his PhD studies. As a result of a number of e-meetings and thanks to the diligence of Mr Prates, I am writing here to confirm that I fully support his application and that I consider that his level of English will be more than sufficient for the requirements of this stage.

Mr Prates intends to spend a stage period in DIT as part of his PhD programme during the summer of 2016. He has chosen DIT in Ireland because of the research expertise in the area kinetic mathematical modelling that he will have available, with the aim to obtain a training that will help him to contribute in the future to Brazilian research.

From my contact with Mr Prates through his previous stage in DIT and during the preparation of this proposal for a stage I have found him to be a very focused researcher who has been trained already in independent work and initiated to research to a high level by the Brazilian Higher Education System.

Mr Prates will be hosted by a research group with more than 15 years experience in the area of shelf life kinetic modelling, with 5 PhD students presently working in research. This will provide an international network to Mr Prates with expertise that will facilitate his training and progress.

In conclusion, I would like to confirm my acceptance of Mr Prates as visiting PhD student under this topic.

Best regards,

Jesús María Frías Celayeta, PhD CFS
Ceann Cúntóir| Assistant Head
Scoil Eolaíocht an Bhia agus Sláinte an Chomhshaoil| School of Food Science and Environmental Health
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SCOIL EOLAÍOCHT AN BHIA & SLÁINTE AN CHOMHSHAOIL /
SCHOOL OF FOOD SCIENCE & ENVIRONMENTAL HEALTH:

October 5th, 2016

To whom it may concern,

This report is on the performance of Mr Pedro Prates Valério during his stay in Dublin Institute of Technology – DIT / School of Food Science and Environmental Health as part of his PhD programme, during the summer of 2016. Mr Prates is a postgraduate student at the Federal University of Minas Gerais – UFMG in Brazil. He came to DIT because of the research expertise in the area kinetic mathematical modelling that he had available, obtaining training that will help him to contribute in the future to Brazilian research.

From my contact with Mr Prates during the preparation of the proposal for the stage, he was a very focused researcher who has been trained already in independent work and initiated to research to a high level by the Brazilian Higher Education System. Mr Prates worked hard during his stay and was able to accomplish quite a lot. The new results should be very helpful for him to fulfil the requirements of a PhD degree at his university. He was also friendly and personable and so was able to work well with the other students and scientists. Pedro Prates Valério was hosted by a research group with more than 15 years experience in the area of shelf life kinetic modelling, with 5 PhD students presently working in research. The experience also provided an international network to Mr Prates with expertise that facilitated his training and progress.

In conclusion, it was a pleasure to have him here, and I look forward to interesting publications resulting from his work. Feel free to contact me if there are any further questions.

Best regards,

Jesús María Frías Celayeta, PhD CFS
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APPENDIX III. Research Papers Submitted and Published in Journals

Valério PP, Cren EC. 2017. A Literature Review of Thermal Degradation Kinetics: Carotenoids in Macauba Oil. Sodebras Journal. 12(141):214–218. ISSN 1809-3957.

A LITERATURE REVIEW OF THERMAL DEGRADATION KINETICS: CAROTENOIDS IN MACAUBA EDIBLE OIL

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Abstract – Recently, the food and chemical industries have been responsible for most of the growing demand for vegetable oils. From the perspective of extractive practices in tropical countries, macauba palm tree enjoys a wide dispersion in Brazil. The industrial interest in macauba has also involved the whole use of its fruit. Considering the interest of consumers and industries in exploring nutraceutical food sources, it is highlighted that the macauba pulp oil contains high amounts of carotenoids. It is reasonable to stand out that the highly unsaturated structures of carotenoid may lead to their functional properties at the same time that creates challenges about its stability during thermal processing. Kinetic models describing carotenoid changes as a function of process parameters are valuable tools for processing optimisation. Thus, kinetic experiments related to macauba oils are recommended to gain further insight into the productive chain.

Keywords: macauba, thermal processing, kinetics

I. INTRODUCTION

Macauba – *Acrocomia aculeata* – is considered a palm tree with greater dispersion in Brazil. Along the last few years, the food industry has been responsible for most of the growing demand for vegetable oils in the world. In this context, the interest in macauba as a food product has been embraced by factors such as the nutritional quality of the edible oils extracted from its edible parts. The pulp and kernel together correspond to approximately 47% (on dry basis) of the total fruit weight. Notably, the pulp contributes to around 60% (on dry basis) of the total edible 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 (PIMENTA et al., 2012, CETEC, 1983).

Fruiting of macauba occurs throughout the year and shows great maturity stage between the months of October and March. In a hectare of Brazilian native land, up to 200 palm trees can be found representing a production close to 25 tonnes of fruit/year, which is notable among other vegetables grown in the country's soil (CAÑO ANDRADE et al.; 2006). FARIAS (2010) points out that the macauba fruit and its derivatives have the quality determined by the association of various attributes, combining physiological factors (*i.e.* level of development and maturity) with physicochemical factors.

Regarding minority compounds, crude macauba oils tend to contain around 5% of non-glyceridic materials. These materials are formed by different quantities of phospholipids, free and esterified sterols, squalenes, phenols, liposoluble vitamins, free fat acids, mono and diglycerides, oxidation products, metals traces, carotenoids, tocols, chlorophyll and other colouring compounds (O'BRIEN, 1998).

Carotenoids and tocopherols are components that stand out among other minority ones due to their antioxidant action and preservation properties. The nutraceutical potential of these both components worth to be mentioned as it highlights the edible oils extracted from macauba as potentially beneficial foods for human health. Especially to the oil extracted from the pulp of the macauba fruit, its colour ranges from yellow to red. This colour is inherently attributed to the presence of carotenoids which concentration can be higher than 300 mg/kg^{-1}. It is important to note that the colour for the kernel oils ranges from white to translucent yellow due to the content of tocols, chlorophyll and also to small amounts of carotenoids (RODRIGUEZ-AMAYA et al., 2008; COIMBRA, 2010; PIMENTA et al., 2012).

Studies on the global food market have indicated new trends and requirements for human feeding by grouping them into five categories: Healthiness and Welfare; Sustainability and Ethics; Pleasure and Sensoriality; Convenience and Practicality; Quality and Reliability. The Brazilian food industry has already indicated the understanding of these new trends and the vegetable oil market has been adapted to consider diversification and value addition for its early production (BARBOSA et al., 2010). It is noticeable that the oils extracted from macauba fruit adhere to the context of health benefits as a feedstock for the production of functional food with special appeals (PIMENTA et al., 2012, CETEC, 1983; PRATES-VALÉRIO et al., 2014).

It is reasonable to stand out that the highly unsaturated structures of carotenoid may lead to their functional properties at the same time that creates challenges about its stability along thermal processings. The compounds are expected to undergo two changes as a result of exposure to high temperature, light, and pro-oxidant compounds: degradation and isomerization (RODRIGUEZ-AMAYA et al., 2008; SAMPAIO et al., 2013). Degradation should be naturally prevented to maintain biological activity. In this sense, quantitative kinetic models describing carotenoid changes as a function of process parameters are valuable tools for process optimisation of vegetable oils including macauba. Carotenoids conversion kinetics is strongly dependent on the food system and compound type. Thus, accurate knowledge on thermal degradation kinetic is

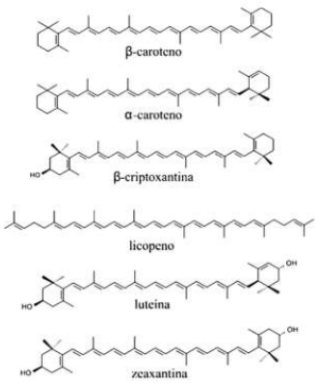
determinant to quantitatively predict specific changes that occur especially in macauba pulp oil (COLLE et al., 2013; RODRIGUEZ-AMAYA et al., 2008; SAMPAIO et al., 2013).

II. THE REVIEW

2.1 – Carotenoids

Accordingly to LEWINSOHN et al. (2005), carotenoids are among the most important pigments in fruits. These tetraterpenes (C40) synthesised by plants are secondary metabolites, essential 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. Carotenoids consist of two classes of molecules: carotenes (hydrocarbons); xanthophylls (contains at least one oxygen function). The β-carotene, which belongs to the first class, is the most widespread in foods. The following Figure 1 shows the chemical structures for some of the mentioned carotenoids that, together with β-carotene, are relevant for human health and feeding.

Figure 1 – Carotenoids with relevance to human health



Source: Rodriguez-Amaya & Kimura, 2008.

Drawing attention to β-carotene, along with α-carotene and β-cryptoxanthin, it is a vitamin A precursor due to its perfect structure of vitamin A dimers. Potentially providing 100% activity, the compound has been highlighted as an important source of vitamin A in developing countries. Indeed, its structure is stoichiometrically equivalent to two molecules of retinol. The molecule can also act as an effective antioxidant because of its highly delocalised electrons which can stabilise intermediates such as carbocations or radicals by resonance reactive. This particular carotenoid can thus protect cellular tissues by quenching singlet oxygen and scavenging active free radicals that are involved in potentially lethal processes, such as lipid peroxidation. (PÉNICAUD et al. 2010).

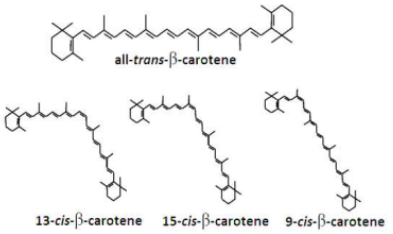
The highly unsaturated structure of β-carotene includes a significant number of double bonds and makes it considerably sensitive to degradation. The β-carotene chemical formula is $C_{40}H_{56}$. It is composed of eight isoprene units (C_5) with specific end groups or two β-ionone rings. The compound is lipophilic, insoluble in water and soluble in organic solvents (*i.e.* petroleum ether, hexane). The β-carotene physical, chemical and biological properties are mainly derived from the mentioned long sequence of conjugated double bonds. Firstly, the single and double bond alternation causes the delocalization of the π electrons and makes the absorption of light possible within the range of the visible spectrum. β-carotene absorbs blue and purple light with a maximal at 450 nm and therefore has an intense red-orange colour (RODRIGUEZ-AMAYA, et al., 2008).

2.2 – Degradation Reactions

In general, carotenoids naturally exist as all-*trans* form. However, as previously discussed, isomerization of all-*trans*-carotene to *cis* forms is one of the major reactions of carotenoids degradation. Therefore, considering that *trans*-β-carotene concentration increases during fruit ripening – including macauba – its level stagnates or tends decrease at post-harvest. Even so, the critical step for the component loss remains related to oil processing as a result of exposure to high temperature, light or pro-oxidant molecules. Indeed, the elevation of temperature during thermal treatment dramatically increases the degradation reactions rates as it varies as a function of temperature (DELLAMONICA & MCDOWELL, 1965; ACHIR et al., 2010; SAMPAIO et al., 2013).

The main degradation products identified after carotenoids and food processing are isomers, oxidation and cleavage products. Current thinking is that the whole process firstly involves isomerization of the all-*trans* to the *cis*-isomer, followed by the formation of a di-radical. The reactions may also occur simultaneously and reversibly. The following Figure 2 illustrates the chemical structures for the most common isomers involved in thermal degradation of carotenoids in vegetable oils systems (ZECHMEISTER, 1962; RODRIGUEZ-AMAYA et al., 2008).

Figure 2 – Isomers: thermal degradation of vegetable oils



Source: Rodriguez-Amaya et al., 2008.

Cis isomers may present residual vitamin A potentials (about two-fold less when compared to *trans isomers*), coloration power and lower antioxidant properties. From the beginning of heating processes 13-*cis*- and 9-*cis*-β-carotene are commonly detected. As well as *trans*-β-carotene, 13-*cis*-β-carotene and 9-*cis*-β-carotene are usually involved in degradation reactions. Thus, it potentially justifies the relevance of monitoring these isomers formation and degradation (ACHIR et al., 2010; ZECHMEISTER, 1962).

2.3 – Carotene Determinations

Along the last few years, the scientific community has invested continuous efforts regarding the correct determination of reliable data related to carotenoids in food. In what it refers to analytical procedures, the uncertainty of

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those that can be used interchangeably for all foods is explained in the complexity of the task itself. Carotenoids are widespread in nature, with different chemical structures and different pro-vitamin potential. Also, concentrations are too varied and happen for different matrices (RODRIGUEZ-AMAYA et al., 2008).

Analytical methods for the determination of carotenoids in complexes matrices are purposed in numerous studies and usually include advanced techniques. In particular for food, trends in the analysis of the mentioned compounds not only reflect the advances in analytical instrumentation but incorporate new knowledge about the role of these compounds in human health. It is well known, however, that advanced techniques are costly. Thus, many analytical procedures have been continually developed with the purpose of establishing simple, rapid and inexpensive procedures for determining carotenoids and pro-vitamins A in foodstuff (TEIXEIRA-GODOY, 1993).

The first methods for determining these pro-vitamin A in food and co-products were based on open column chromatography (OCC) technique. The latest methods are based on High-Performance Liquid Chromatography (HPLC) as well as on related practical techniques: Ultra Performance Liquid Chromatography, Mass Spectrometry, among others (TEIXEIRA-GODOY, 1993).

Under the chemical aspect, it is important to mention that the saponification is a procedure to be included before chromatography which has been applied to remove unwanted lipids and chlorophylls, eventually hydrolyzing carotenoids esters. This operation, however, is included only when necessary as it extends the time of analysis and can promote the formation of artefacts and degradation of carotenoids (TEIXEIRA-GODOY, 1993).

Because carotenoids absorb maximally at different wavelengths and have different absorption coefficients, some results obtained from normalisation (area percentages) can only be taken as approximate relative proportions. For food science and nutrition purposes, however, these results are useful if presented regarding concentration, that is, the weight of the pro-vitamin per unit weight of the sample. It can thus be done in HPLC using internal or external calibration curves, for which the concentrations of the standards are also determined spectrophotometrically. It is emphasised that analytical methods for the determination of total carotene content may be suitable to the nature of each sample. This suitability is one of the main requirements for obtaining reliable data on carotenoids. In this context, among other minimum criteria, particularly related to spectrophotometric identifications of carotenoids, there is a need to correctly set the absorption spectrum in the adequate UV-VIS region of the compound to be determined (RODRIGUEZ-AMAYA, 1997; DAVIES; 1976).

The value of vitamin A in food can be determined based on what is called "β-carotene fraction" or "total carotene". The method is recommended by the AOAC (DEUTSCH, 1990). Nevertheless, the mentioned method is appropriate only when β-carotene is both the most widely distributed carotenoid and the most active pro-vitamin A in the analysed food and co-products – as it occurs for macaúba oils. Thus, for food in which the fraction of β-carotene becomes smaller compared to that of other active carotenoids, the result can be overestimated. On the other hand, if active carotenoids are not included in this fraction, the result can be underestimated – i.e. papaya, cashew and pumpkin (RODRIGUEZ-AMAYA, 1989; GODOY & RODRIGUEZ-AMAYA, 1993).

2.4 – Degradation Kinetics

Along with products identification, kinetic data on thermal degradation are necessary to predict carotene loss during processing. In this sense, kinetic evaluation is required to derive necessary kinetic information for a system to describe the reaction rate as a function of experimental variables as well as to predict changes in a particular food system during processing. In general, most of the studies in real food report a first order reaction (ZAO, 2011; DONG-SUN & HYUN-KU, 1989; HENRY et al., 1998; AHMED, SHIVARE & SANDHU, 2002) on the concentration of *trans*-β-carotene in different systems at different temperatures. Although zero-order equations have also been verified, the use of a first-order kinetic is realistic in most cases (PÉNICAUD et al. 2010).

Some studies tested superior reaction orders by linearization methods or non-linear regression and found a better fit of experimental data with orders superior to one for *trans*-β-carotene degradation in non-polar solvents. The superior orders may be explained by the competition with isomerization reactions which are of importance in vegetable oils. The majority of the kinetic models used to describe *trans*-β-carotene degradation are single response kinetic models. However, as the compound is supposed to degrade in various products, the real reaction scheme is complex and of high dynamics (PÉNICAUD et al. 2010; SAMPAIO et al., 2013; ACHIR, et al., 2010; CRANDALL, KESTERSON & DENNIS, 1983).

Regarding the estimation of kinetic parameters for *trans*-β-carotene degradation, the rate constants k (s^{-1}) tends to vary ranging from 0.00018 (120° C) to 0.0015 (180° C). The apparent activation energy Ea (kJ.mol-1) tends to range from 80 to 110 (DHUIQUE-MAYER et al., 1997; HENRY, CATIGNANI & SCHWARTZ, 1998; SAMPAIO et al., 2013; ACHIR, et al., 2010; CRANDALL, KESTERSON & DENNIS, 1983). The rate constants (k) are assumed to vary according to the Arrhenius law as the temperature dependence is often given by the related equation 1.

$$k = k_0 * \exp(-E_a/RT) \quad (1)$$

Where,
k = Specific Rate Constant
k_0 = Pre-Exponential Factor
E_a = Activation Energy (J mol^{-1})
R = Gas Constant (8.314 J.mol^{-1} K^{-1})
T = Absolute Temperature (K)

Predominantly, experimental data are mainly presented in functions of C and C_0 at different heating time intervals t, where C is the carotenoid concentration (mg/kg of oil) at each time t and C_0 is the amount of carotenoid when the trial reaches the desired temperature (isothermal temperature). The following differential equation (2) is general and largely applied for carotenoid changes (SAMPAIO et al., 2013).

$$dC/dt = -k*C\hat{}n \quad (2)$$

The presented equation (2) conveys that the degradation rate dC/dt is proportional to the n^{th} power of carotenoids concentration (C in mg/kg of oil) at any time t, while n is the

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order of the reaction and k (1/time) is the reaction constant (SAMPAIO et al., 2013).

In a research carried on by ACHIR et al. (2010) a kinetic approach of *trans*-β-carotene is presented in enriched vegetable oils. The study highlights different thermal sensitivities depending on carotenoids type and shows the influence of the original oil quality and composition on carotenoid degradation. The authors affirm that low peroxide value and high tocol content can limit carotenoid oxidation. In conclusion, it is recommended to work at low temperature for a long time instead of a high-temperature-short-time treatment.

COLLE et al., (2013) compare the thermal degradation and isomerization of β-carotene and lycopene in different food systems. To study the degradation reaction, a single response modelling approach was used, while multi-response modelling was applied to describe isomerization reactions and products: 13-*cis*-β-carotene, 9-*cis*-β-carotene and 15-*cis*-β-carotene. In conclusion, the study clearly shows that carotenoids conversion kinetics are strongly dependent on the carotenoid type as well as on the food system. It is affirmed that process optimisation demands specific kinetic data.

ZEPKA et al. (2009) proposed a multi-response model to represent carotenoid degradation in cashew apple juice. Considering simultaneous apparition and disappearance of intermediary products, the mechanism involves parallel irreversible and reversible reactions of *trans*-β-carotene to yield mono-*cis*-isomers. Therefore, as a result of the products global monitoring, the authors determined different constant rates, discriminating two pathways and evaluating the effect of temperature supply on carotenoid degradation.

III. CONSIDERATIONS

Over the last decades, the vitamin A deficiency has been recognised as a major public health problem in developing countries. In this context, the interest in macauba (*Acrocomia aculeata*) as a food product is embraced by the nutritional quality of its edible oils. Carotenoids give to crude macauba pulp oil the distinctive orange-red colour. Therefore, together with tocopherols, the mentioned tetraterpenoids contribute to the stability and nutraceutical value of this edible oil. Recently, industries have shown a growing interest in exploring the potential of several functional raw materials. Under the referred circumstances, it shall be noted that the nutritional quality of macauba oils becomes strongly dependent on processing steps. Isomerization and Oxidation are the two most important reactions of carotenoids degradation that occur during edible oil processing. Thus, kinetic models describing carotenoid quantitative changes as a function of process parameters are valuable tools for oil processing optimisations. Carotenes degradations are highly dependent on many factors linked to the medium in which they are contained. Usually, studies mainly deal with β-carotene degradation, and only a few kinetic parameters are currently available. Furthermore, experimental variabilities summed to the scarcity of information under the heating conditions make data difficult to compare. The lack of kinetic data related to macauba edible oils is also highlighted. Kinetic models used to describe carotenoids degradation are usually single response. In general, most of the studies about *trans*-β-carotene degradation in oil systems report a kinetic behaviour outlined by first-order reactions. Superior reaction orders may explain the competition between isomerization-oxidation reactions of carotenoids degradations. Hence, specific experiments regarding macauba oils are strongly recommended to gain further insight into the productive chain of the crop and the carotene reactivity over a broad temperature range. Kinetic modelling considering dynamic behaviour may achieve innovation.

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KINETIC PREDICTIONS OF TOTAL CAROTENOIDS RETENTION IN MACAUBA OIL UNDER INTERESTERIFICATION CONDITIONS

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***Abstract* – Recently, the world consumption of palm oils has increased significantly. Under the perspective of industrial applications, several processes are conducted to modify native vegetable oils to meet functional performances of structured lipids. In this sense, the recent scientific and technological advances related to interesterification open up perspectives for new products and processes developments. Macauba oils are, thus, presented as alternative raw materials for industrial purposes that also include interesterification. This study was undertaken with the primary objective of considering conventional processing conditions applied for the interesterification of vegetable oils to kinetically predicting the thermal effects on the retention of natural carotenoids in the macauba pulp oil. Different previous studies give the kinetic parameters. The retaining of the bio-compounds for producing structured lipids with special appeals is highlighted.**

Keywords: carotenoids, kinetics, interesterification

I. INTRODUCTION

The world consumption of vegetable oils increased significantly in recent years (USDA, 2016; GRAHAM-ROWE, 2011; DA SILVA, 2013). Along the period between 2008 and 2017, this consumption has also been driven by food production to represent a growth of around 43%, reaching 183 million metric tonnes. The world consumption of palm oils followed the mentioned increased to represent 35% of the global volume registered in 2017 (USDA, 2017).

Under the perspective of industrial applications, several processes are proposed to modify native vegetable oils. These modifications are usually conducted to meet functional performances of structured lipids, including plasticity, tractility and shortening property (XIE, YANG & ZANG, 2015; XU, 2000). Among the most commonly applied methods to tailor physicochemical properties of edible oils, interesterification has received much attention. Unlike hydrogenation, interesterification processes are not related to the formation of trans fatty acids in final products. Therefore, interesterification methods potentially extend the commercial application of modified lipids to the production of a wide variety of foodstuffs (GIBON, 2011).

It is important to highlight that interesterification process of vegetable oils are usually carried out chemically or enzymatically. Both reactions promote rearranges in the distribution of the fatty acids located in the triacylglycerol structures, preserving the fatty acids profiles. The process consists of simultaneous ester breakages with the formation of new aleatory bonds (COSTALES-RODRIGUEZ, 2009).

It is emphasised that chemical interesterification is a widely applicable process in which the low-acid vegetable oils are not required to be previously bleached. Being inexpensive when compared to enzymatic interesterification, the method is amenable to be scaled up and also considered efficient, relevant and feasible in the edible oil industry (OSBORN & AKON, 2002; SCRIMGEOUR & HARWOOD, 2007).

Under the perspective of industrial processes, chemical interesterification is carried out considering homogeneous base catalysts, typically sodium methanolate $NaOCH_3$ (DIJKSTRA, 2015; MARANGONI & ROUSSEAU, 1995; RODRIGUEZ et al., 2001). Although these catalysts are robust and low-cost, the need for their inactivation and removal at the end of each process is required. Thus, attention is deserved regarding possible contaminations of structured food lipids (SOARES et al., 2012). Consequently, besides reducing oil yield, the necessity of eventual post-treatments steps (*i.e.* bleaching, deodorization) can contribute to increasing processes costings also removing valuable micronutrients naturally present in native vegetable oils (DIJKSTRA, 2015).

In this framework, heterogeneous catalysts have received recent attention as a way of overcoming drawbacks related to homogeneous interesterification. These catalysts contribute with several industrial advantages which include high catalytic activity, easiness of separation and recyclability. In this sense, heterogeneous interesterification is shown to apply to reduce post-treatments steps also enabling the retention of bio-compounds in final structured lipids. By consequence, the method apparently opens up perspectives for new processes development also related to special food productions. Indeed, the potential of the method to meet food specifications has already been shown (DIJKSTRA, 2015; XIE & XEN, 2014; XIE & QI, 2013).

It is certain that successful synergies in the current scenario require a focus on specific contextual problems and opportunities. In this sense, it should be observed that consumers have recently shown an increasing demand for natural products from the food industry (CATALDO et al., 2016; BABBAR et al., 2015; GONÇALVES et al., 2014). It is noted that the consumption of these products tends to be associated with the health-related benefits obtained from bioactive compounds, among which fatty acids, carotenoids and micronutrients constitute important classes (JUÁREZ-HERNÁNDEZ et al., 2016; BABBAR et al., 2015; LIM & KIM, 2016).

In this scenario, macauba (*Acrocomia* aculeata) is presented as an alternative crop for purposes that also include interesterification processes. Macauba is one of the most widespread palms in the Neotropics (UHL &

DRANSFIELD, 1987; SCARIOT et al., 1995). With a similar productive potential to *Elaeis guineensis* (FAO, 2013; EVARISTO et al., 2016) it is suited to edaphoclimatic zones, which feature conditions averse to African palms (LANES et al., 2016).

An adult macauba palm fructifies almost the whole year with productivity from 4 to 9 tonnes of esculent oil per hectare. Regarding the oil extracted from the pulp, it is readily edible and contains up to 378 mg/kg of carotenoids. The pulp oil has a predominance of unsaturated fatty acids (77%) of which 53% and 18% are oleic (ω-9) and linoleic (ω-6), respectively. The edible oil extracted from the kernel has a predominance of saturated fatty acids (74%), of which 44% and 9% are lauric and palmitic, respectively (NUNES et al., 2012; CETEC, 1983).

Notably, the macauba fruit provides two different types of edible oils which can be suggested to be used together as raw materials for the production of structured lipids. In fact, industrial efforts have already become remarkable in the sense of producing different blends of vegetable oils to enhance the nutritional characteristics of structured lipids with specific functional properties (GRIMALDI, GONÇALVES and ANDO, 2005; NORIZZAH et al., 2004; RODRIGUEZ et al., 2001; PETRAUSKAITE et al., 1998; LIDA & ALI, 1997).

Thus, the present study was undertaken with the primary objective of considering conventional processes conditions applied for the interesterification of vegetable oils to kinetically predicting the thermal effects on the retention of natural carotenoids in the macauba pulp oil.

II. PROCEDURES

2.1 – Fruit Pre-processing

Macauba fruit was collected from native palms with a maximum of five days after the fall in the area of the Federal University of Minas Gerais, in the metropolitan region of Belo Horizonte, Minas Gerais, Brazil. The macauba mesocarp and kernel were promptly separated from the fruit. Before the oil extraction, these parts were thawed, air dried at 60° C for 48 hours and comminuted in an electric grinder coupled to a stainless steel cup (PIMENTA, 2010; GOULA, 2013). The mesocarp and kernel pressings were performed on different days, avoiding any cross-contamination.

2.2 – Oil Processing

The samples consisted of edible oils mechanically obtained from the pulp and kernel of macauba fruit by continuously operated *Expeller*® press. 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 until the analysis (PREEDY, 2014; PARDUCCI & FENNEMA, 1978).

2.3 – Determination of Fatty Acid Compositions

The fatty acids compositions were determined based on the methods previously optimised by CHRISTIE (1989) and GUO et al. (2011). The analysis was carried out on a GC-2010 System (Shimadzu, Japan) fitted with a Flame Ionization Detector. Quantification of individual fatty acids methyl esters – FAME considered a standard mixture of 37 esters of fatty acids (Supelco, Bellefonte, Pa., USA).

2.4 – Determination of Acid Value

The Acid Value (AV) for the macauba pulp oil was determined according to the AOCS Official Method 3d Cd-63 (AOCS, 2009). The determinations were performed by diluting 1 g of oil in 50 mL solution of isopropanol:toluene (1:1) followed by titration with potassium hydroxide (0.1 mol/L) standardised with potassium biphthalate. The AV were calculated by the equations (1) and (2).

$$AV\ (mg\ KOH.g^{-1}) = (A–B)xMx56.1/W \quad (1)$$

$$AV\ (\%\ oleic\ acid) = (A–B)xMx28.2/W \quad (2)$$

Where,
A = KOH volume (mL) used for the sample titration
B = KOH volume (mL) used for the blank titration
M = Molarity of the base, after standardisation
W = Weight (g) of the sample

2.5 – Spectrophotometric Determination: Total Carotenoids

The spectrophotometric determination of the initial concentration of total carotenoids occurred using a Hach DR 2800 spectrophotometer (Hach, Loveland, CO, USA) as recommended by RODRIGUEZ-AMAYA & KIMURA (2004) and suggested by PORIM (1990). The quantification ($mg.kg^{-1}$) considered an absorption coefficient ($A^{1\%}_{1cm}$) of 2580 in high purity n-hexane (ZSCHEILE et al., 1942).

2.6 – Kinetic Prediction: Total Carotenoids retention

In order to predict the retention of total carotenoid in the macauba mesocarp oil, the processing parameters related to the interesterification were defined based on GRIMALDI, GONÇALVES & ANDO (2005), NORIZZAH et al. (2004), RODRIGUEZ et al. (2001), PETRAUSKAITE et al. (1998) and LIDA & ALI (1997). The isothermal temperature (DINH, SUN & MCLEAN, 2016) of 120 °C was considered along the processing time of 120 minutes.

The prediction of the carotenoids retention was carried out using MS Excel software, version 16.0.6001.1070 (Washington, USA). The different kinetic parameters used to evaluate the maintenance of total carotenoids in the macauba pulp oil are given by ACHIR et al. (2010), HENRY, CATIGNANI & SCHWARTZ (1998), APARICIO-RUIZ & MÍNGUEZ-MOSQUERA (2011) and KNOCKAERT et al. (2012) and compared considering the presented processing parameters. The first-order kinetic model was considered appropriate for predicting the total carotenoids retention in macauba vegetable oils. The lack of data related to the thermal degradation of carotenoids in macauba oils is noted.

The kinetic predictions considered data obtained from the following equation (3) being expressed relative to the initial concentration of carotenoids as a function of time:

$$P_{carot} = \exp(-k_{ref}*\exp(-Ea/R*(1/(T_{ref})-1/T_{ref}))*time) \quad (3)$$

Where,
T_{ref} = Absolute Processing Temperature (K)
k_{ref} = Specific Rate Constant given by literature
Ea = Activation Energy ($J\ mol^{-1}$)
R = Gas Constant ($8.314\ J.mol^{-1}\ K^{-1}$)
P_{carot} = Prediction as a function of time

The rate constant (k, min^{-1}) was assumed to vary with the absolute temperature T (K) according to Arrhenius law

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(FOGLER, 2016). In this sense, the reparametrized equation (4) was considered to estimate the rate constant (k) at the defined processing temperature.

$$k = k_{ref}*\exp(-Ea/R*((1-T)-(1/T_{ref}))) \quad (4)$$

Where,
T_{ref} = Absolute Reference Temperature (K)
k_{ref} = Rate Constant at the Reference Temperature
k = Specific Rate Constant
Ea = Activation Energy (J mol^{-1})
R = Gas Constant (8.314 $J.mol^{-1}$ K^{-1})

As a definition, it is worth noting that the equation (5) is normally given for the study of carotenoids changes:

$$dC/dt = -k*C\text{^}n \quad (5)$$

The presented equation (4) conveys that the degradation rate dC/dt is proportional to the n^{th} power of carotenoids concentration (C in mg/kg of oil) at any time t, while n is the order of the reaction and k (1/time) is the reaction constant.

III. RESULTS

3.1 – Results for the Fatty Acid Composition

Table 1 shows the mean and standard deviation for the fatty acid composition (expressed as a percentage of total fatty acids) for the macauba pulp and kernel oils.

Table 1 – Fatty acid composition of macauba pulp and kernel oils expressed as percentage of total fatty acids

Fatty Acid	Macauba Palm	
	Pulp Oil	Kernel Oil
Caproic acid (C6:0)	ND	0.35 ± 0.00
Caprylic acid (C8:0)	0.08 ± 0.05	4.38 ± 0.04
Capric acid (C10:0)	ND	3.62 ± 0.03
Undecylic acid (C11:0)	0.08 ± 0.04	ND
Lauric acid (C12:0)	0.04 ± 0.01	37.22 ± 0.03
Myristic acid (C14:0)	0.07 ± 0.00	8.12 ± 0.02
Pentadecylic acid (C15:0)	0.17 ± 0.00	0.03 ± 0.00
Palmitic acid (C16:0)	19.62 ± 0.56	6.88 ± 0.02
Palmitoleic acid (C16:1)	1.68 ± 0.04	0.16 ± 0.01
Margaric acid (C17:0)	0.09 ±0.00	0.04 ± 0.00
Ginkgolic acid (C17:1)	0.06 ± 0.00	0.04 ± 0.00
Stearic acid (C18:0)	5.15 ± 0.17	2.90 ± 0.02
Oleic acid (C18:1)	60.33 ± 1.18	32.0 ± 0.01
Linoleic acid (C18:2)	8.81 ± 0.32	3.94 ± 0.02
α-Linolênic acid (C18:3)	0.73 ± 0.02	0.06 ± 0.00
Arachidic acid (C20:0)	0.21 ± 0.00	0.14 ± 0.00
Gadoleic acid (C20:1)	0.07 ± 0.01	0.14 ± 0.01
Behenic acid (C22:0)	0.14 ± 0.01	0.09 ± 0.01
Eicosadienoic acid (C20:2)	1.83 ± 0.46	ND
SFA	25.65 ± 0.84	63.75
MUFA	62.11 ± 1.23	32.32
PUFA	11.37 ± 0.80	3.93

It can be observed the predominance of oleic acid in the macauba pulp oil. Importantly, the level is similar to those (48-74%) of palm stearin (CODEX, 2015), which is widely used for interesterification purposes. The palmitic acid was the second most abundant fatty acid in the pulp oil, in agreement with previous reports (HIANE, 2005; NUNES et al., 2015; CETEC, 1983). Lauric acid was the predominant fatty acid in macauba kernel, what also occurs to other palm crops such as babassu and the kernel oil, kernel olein and kernel stearin of *Elaeis guineensis* (CODEX, 2015).

The predominance of unsaturated fatty acids (MUFA: 62.11 ± 0.84%; PUFA: 11.37 ± 1.23%) was observed for the pulp oil. On the other hand, the predominance of saturated fatty acids became apparent for the kernel oil (SFA: 63.75 ± 0.84%). Regarding the ω-6 family of fatty acids, the linoleic acid in the macauba pulp (8.81%) and kernel (3.94%) oils were similar to those reported (CODEX, 2015) for palm oil (9.0-10%), palm stearin (3.0-10%), sunflower oil (2.1-17%) and virgin and refined olive oils (3.5-21%). The contents of linoleic acid in the macauba oils were, yet, higher than those registered for palm kernel oil (1.0-3.5%), palm kernel olein (2.4-4.3%) and palm kernel stearin (0.5-1.5%).

The clear distinction between the fatty acid profiles of macauba pulp and kernel oils, especially regarding the contents of saturated and unsaturated fatty acid, already renders it an important role as a potential alternative oil crop for interesterification purposes. Indeed, the fatty acid compositions of these two types of oils are similar to that of other broadly used raw materials mainly blended to meet and improve functional performances of structured lipids (XIE, YANG & ZANG, 2015; XU, 2000).

3.2 – Results for Acid Value and Total Carotenoids

The following Table 2 shows the mean and standard deviation for the Acid Values in the macauba pulp oil, also presenting the initial content of total carotenoids determined spectrophotometrically.

Table 2 – Acid value and total carotenoids: macaúba pulp oil

Determinations	Pulp Oil
Acid Value (mg $KOH.g^{-1}$)	1.6 ± 0.1
Acid Value (% oleic acid)	0.8 ± 0.1
Total Caroteniod (mg/kg)	234.9 ± 2.9

As it can be seen, the contents of free fatty acids – FFA were well bellow the limit of 4.0 mg $KOH.g^{-1}$ established by the Resolution RDC 270, of the Brazilian Health Regulatory Agency – ANVISA (Brasil, 2005), for cold, pressed and non-refined vegetable edible oils. It is highlighted that the acid value has already been widely determined in literature for the macauba kernel oil (CETEC, 1983; PIMENTA, 2010; COIMBRA & JORGE, 2011; HIANE et al., 2005). It has been, therefore, observed that the free fatty acids in kernel oils range from 0.3 to 0.7 (mg $KOH.g^{-1}$) which are usually much lower than that of pulp oils. In fact, lipolytic enzymes catalyse the decomposition of triglycerides and tend to be mostly active in pulps (COIMBRA & JORGE, 2011).

Above all, low values of acidity observed for macauba pulp and kernel oils adheres to interesterification purposes (OSBORN & AKON, 2002; SCRIMGEOUR & HARWOOD, 2007) reinforcing the macauba oils as raw materials for industrial uses.

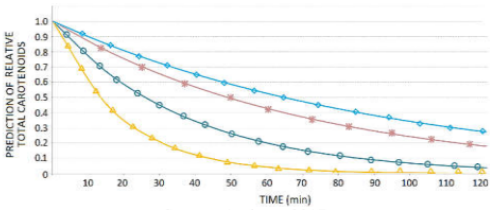
Regarding total carotenoids in the macauba pulp oil (234.9 $mg.kg^{-1}$) the content surpasses of other tropical fruits becoming one of its remarkable characteristics (RUFINO et al., 2010; RODRIGUEZ-AMAYA, KIMURA & FARFAN, 2008). Consistent with our observations, NUNES et al. (2015) and COIMBRA & JORGE (2011) reported the crude macauba oil to contain above 300 $mg.Kg^{-1}$ of total natural carotenoids. Wherefore, although some variability in the carotenoid content tends to be noted for different macauba genotypes, it is suggested that, once preserved in final products, these bio-active compounds may enrich the

composition of structured lipids derived from macauba oil to compete against products that don't have that natural appeal (CATALDO et al., 2016, BABBAR et al., 2015; GONÇALVES et al., 2014).

3.2 – Kinetic Prediction of Carotenoids retention

The kinetic predictions of the thermal effects on the retention of natural carotenoids in the macauba pulp oil are presented in Figure 1. The results are expressed relative to the initial concentration, as a function of time.

Figure 1 – Prediction of thermal effects on the retention of natural carotenoids in the macauba pulp oil, expressed relative to the initial concentration as a function of time: ACHIR et al. (2010) – filled diamond, HENRY, CATIGNANI and SCHWARTZ (1998) – filled triangle, APARICIO-RUIZ & MÍNGUEZ-MOSQUERA 2011) – filled circle and KNOCKAERT et al. (2012) – filled star.



Source: Authors, 2017.

It is observed that the extreme conditions (2 h at 120 °C) similar to those of interesterification appeared to significantly decrease the initial amount of total carotenoids in the macauba pulp oil. Notably, the total carotenoids were reduced by at least around 70% and 80% when considering the kinetic parameters (apparent activation energies and rate constant) given by ACHIR et al. (2010) and KNOCKAERT et al. (2012), respectively.

A further comparison considering all the predictions showed that after 50 minutes at least around 40% of the total carotenoid might have been degraded as a consequence of temperature supply. It leads to verify that around 118 mg/kg of carotenoids would may remain in the macauba pulp oil after this processing time. Importantly, as expected, the dimensionless concentrations of carotenóids always decreased as a function of heating time, independently of the kinetic data used for the prediction.

Indeed, from the perspective of industrial thermal processing, the highly unsaturated structures of carotenoids does make the compounds considerably sensitive to thermal degradation reactions (FAO, 1995, ACHIR et al., 2010). Moreover, rates of the carotenoids degradation reactions have been reported to dramatically increase during different thermal treatments varying with increases of temperature (ACHIR et al., 2011; DELLAMONICA & MCDOWELL, 1965). It is, therefore, noted that the temperature intensity is an important factor to be controlled along the processes regarding total carotenoid retentions in macauba oil

It can also be observed (Fig. 1) a significant variability between the predictions. In fact, if we carefully analyse the data given by previous studies, it is possible to verify quantitative differences in the kinetic data provided by different authors. This comparison may indicate that carotenoids degradation appears to be complex and highly dependent on factors linked to the food systems and the matrix they are studied. In this sense, it is stated that studies considering the thermal degradation kinetics of carotenoids in macauba oil are imperative for obtaining data even more reliable for future contributions. Particularly in engineering, kinetic data also is used for designing products, efficient processes and large scale reactors. Thus, kinetic studies that aim knowledge and understanding on the thermal degradation of bioactive compounds, such as carotenoids, naturally present in macauba oils may adequately probe its function.

IV. CONCLUSION

This study reinforces macauba pulp and kernel oils as alternative raw materials for industrial purposes, including interesterification. The joint use of the two mentioned oils is in agreement with the already existing efforts for producing different blends of vegetable oils to enhance the nutritional characteristics of structured lipids with specific functional properties. It is noteworthy that macauba oils are also presented with functional properties (*e.g.* fatty acid profiles) similar to those of products derived from African palm. The kinetic predictions carried out in this study made it possible to evaluate possible thermal effects on the retention of natural carotenoids in the macauba pulp oil. The predictions considered previously published processing conditions that may similarly occur for interesterification methods. The retaining of naturally present bio-compounds, such as carotenoids, in macauba for producing structured lipids with special appeals is highlighted as recent scientific and technological improvements related to interesterification processes open up perspectives for new products and processes developments. Additionally, taking into account that carotenoids degradation is highly dependent on factors linked to the food system in which they are contained, this study suggests that specific knowledge on the estimation of kinetic parameters in macauba oils is imperative for obtaining data even more reliable for future contributions and for accurate predicting specific changes that may occur during the industrial processing of the raw materials.

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Valério PP, Cren EC. 2017. Thermal Degradation Kinetics: Carotenoids Influencing Macauba Mesocarp (*Acrocomia aculeata*) Oil Attribute. Journal of Food Science, IFT. ISSN 1750-3841. Manuscript Number: JFDS-2017-1495.

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APPENDIX IV. Scientific Studies Published in Annals of Research Events

4th International ISEKI_Food Conference: Responsible Research and Innovation in the Food Value Chain. Vienna, Austria. 2016.

Valério PP, Cren EC. 2016. A parallel between the degradation of beta-carotene and hydrolytic reactions in macauba palm oil.

Abstract: The final quality of edible vegetable oils is strongly dependent on processing steps. Once the free fatty acid content (FFA) is usually related to the degradation of triacylglycerol by a hydrolysis reaction, the acid value represents a quality indicator for vegetable oils. The mentioned reaction tends to occur during the storage, as well as during the oil pre-treatments and extraction processes. It is important to note that the higher the content of FFA, the lower the oil Yield – and more expensive become the subsequent oil processes (i.e. refining). The processing of vegetable oils in the presence of water and under the action of high temperatures tends to show increases in the content of FFA and decreases in oxidative stability. The free radicals are the centrepieces of oxidative reactions in lipids. In this context, β-carotene is a highly unsaturated molecule containing conjugated double bonds in its chain. It is thus well known that these tetraterpenoids naturally present in crude macauba mesocarp oil (100 - 378 $mg.kg^{-1}$) are very susceptible to the attack of a lipid radical or of oxygen at the oil/air interface. This attack leads to the production of a carotenoid-peroxyl radical which takes part in degradation and cleavage reactions of both β-carotene and unsaturated lipids. Experiments carried out on crude macauba mesocarp oil, along eight months period of storage (at room temperature, under light protection), showed increases of at least 42% for the content of FFA (mg $KOH.g^{-1}$) accompanied by a decrease of at least 25% for the β-carotene content ($mg.kg^{-1}$). It is reasonable to note that the pro-vitamin A degradation reaction also seems to go parallel to the hydrolytic reactions of unsaturated lipids. Thereby, the deepening of issues relating hydrolytic reactions in nonpolar mediums and carotenoid degradation along the storage of macauba raw materials may be of interest.

Keywords: β-carotene, hydrolytic reaction, macauba, vegetable oil

4th International ISEKI_Food Conference: Responsible Research and Innovation in the Food Value Chain. Vienna, Austria. 2016.

Valério PP, Cren EC. 2016. An approach on thermal degradation kinetics of carotenoids in macauba pulp oil.

Abstract: Over the last decades, the vitamin A deficiency has been recognised as a major public health problem in developing countries. In this context, the interest in macauba (*Acrocomia aculeata*) as a food product is embraced by the nutritional quality of its edible oils. Carotenoids give to crude macauba mesocarp oil its distinctive orange-red colour (100 – 378 mg β-carotene.kg^{-1}). Therefore, together with tocopherols, the mentioned tetraterpenoids contribute to the stability and nutraceutical value of this oil. Industries have shown a growing interest in exploring the potential of functional raw materials. Under the circumstances, it shall be emphasised that the nutritional quality of macauba oils is strongly dependent on the processing steps. Isomerization and oxidation are the two primary reactions of carotenoids degradation that occur during edible oil processing. Thus, kinetic models describing carotenoid quantitative changes as a function of process parameters are valuable tools for oil processing optimisation. Carotenes degradations are highly dependent on many factors linked to the medium in which they are contained. Studies mainly deal with β-carotene degradation, and only a few kinetic parameters are currently available. Furthermore, the experimental differences and the scarcity of information under the heating conditions – the lack of kinetic data for macauba oils is worth of mentioning – make data difficult to compare. Kinetic models used to describe β-carotene degradation are usually single response. In general, most of the studies about β-carotene degradation in palm oil (*Elaeis guineensis*) report a kinetic behaviour described by first-order reaction: k (x 10^{-4} s^{-1}) tends to range from 1.8 (393.15 K) to 15.0 (453.15 K); E_a (kJ.mol^{-1}) 83. Superior reaction orders might explain the competition between isomerisation/oxidation reactions of carotene degradation. Hence, additional experiments in macauba oils are recommended to gain further insight into the carotene molecule reactivity over a broad temperature range. Kinetic modelling considering dynamic behaviour may achieve innovation.

Keywords: edible vegetable oils, carotenoids, kinetic modelling, thermal degradation

IUFoST - 18th World Congress on Food Science and Technology. Dublin, Ireland. 2016.

Valério PP, Celayeta JMF, Cren EC. 2016. The potential of macauba fruit (*Acrocomia aculeata*) from the perspective of functional food production and environmental sustainability.

Abstract: Recently, the food and chemical industries have been responsible for most of the growing demand for vegetable oils. From the perspective of extractive practices in tropical countries, macauba palm tree enjoys a wide dispersion in Brazil. From the point of view of sustainability, the industrial interest in macauba has involved the whole use of its fruits which have generated different co-products, beyond oils, adding value to the waste stream of oil processing: e.g. activated coal (endocarp); vegetable coal – high calorific value (endo/exocarp); human food and animal feed (mesocarp and kernel bran), among others. Analytical experiments carried out at UFMG have shown that the macauba mesocarp and kernel together account for approximately 47% of the fruit total weight, which contain 50% of oil (dry basis). The fatty acid composition of the mesocarp has been found to have a predominance of beneficial unsaturated fatty acids (73.99%; oleic acid: 60%). On the other hand, the macauba kernel has a predominance of saturated fatty acids (63.65%; lauric acid: 37%). Results obtained on the natural content of total carotenoids (100 – 340 $mg.kg^{-1}$) and tocols (45 – 85 $mg.kg^{-1}$) show the functional potential of macauba oils. The β-carotene represents from 50% to 80% of total carotenoids in macauba mesocarp; together with tocopherols (44 $mg.kg^{-1}$), the mentioned hydrocarbon contributes to the stability and nutraceutical potential of edible macauba oils. Considering the growing interest of consumers and industries in exploring nutraceutical food sources, the whole use of the macauba fruit also brings up its potential for sustainable food processes.

Keywords: *Acrocomia aculeata*, edible oils, sustainability, industrial processing

XXI COBEQ – Brazilian Congress of Chemical Engineering. Fortaleza, Brasil. 2016.

Valério PP, Cren EC. 2016. Progression of FFA content in crude macauba oils stored under light protection and temperature monitoring.

Abstract: The final quality of edible vegetable oils tend to be strongly dependent on processing steps related to such raw materials. Particularly, these steps usually range from post-harvest handlings – including cleaning, transport and storage – to the oil processing stages – extraction, refining, storage and distribution. Regarding acidity value as a quality parameter, its relation to the degradation of triacylglycerol by hydrolysis reaction is widely known. Moreover, once the mentioned reaction also occurs along storage periods, as well as during pre-treatments and extraction processes, it is reasonable to suggest that the higher the Free Fatty Acid content (FFA) in vegetable oils, the more expensive may to be the refining process. It thereby can cause reductions in edible oil yield and directly affects co-products shelf life. In this way, this study aimed to analyse the progression of the free fatty acid content in crude Macauba oils – mechanically extracted from the mesocarp and kernel of fresh *A. aculeata* fruit, at different processing conditions – stored under light protection and monitored temperature. An increase of at least 42% in the content of FFA was registered for the mesocarp oils and of at least 15% for the kernel oils (period of storage: 8 months). The methodology used to determine the acidity was based on the official method Ca 5a-40, of the American Oil Chemists' Society. The results obtained in this study allowed observing evidence on the relationship between extraction conditions and conservation of FFA contents. Additionally, the harvest and post-harvest handling were strengthened as important factors to avoid intense hydrolysis reaction of triglycerides in macauba oils, helping to keep the relatively low acidity of samples, consequently increasing product stability. This support the feasibility of commercial exploitation of high-quality macauba mesocarp oil as a convenient source of raw material for the oleochemical industry.

Keywords: free fatty acids, hydrolysis reaction, crude macauba oils

XX COBEQ - Brazilian Congress of Chemical Engineering. Florianópolis, Brasil. 2014.

Valério PP, Grande SC, Caño-Andrade MH, Cren EC. 2014. Perspectives for a novel food product considering of the oils obtained from fresh macauba fruit (*Acrocomia aculeata*).

Abstract: The present study envisages the use of esculent oils mechanically extracted from macauba fresh fruits as value-added raw materials for food production. The research work presents a literature review that contemplates physicochemical properties and quality characteristics of vegetable oils obtained for food purposes – among which those extracted from the olive tree (*Olea europaea*) and African palm (*Elaeis guineensis*). Technical regulations, as well as recommended international standards and official methodologies, are collated. The study, therefore, contributes to the definition of processing parameters for macauba, in order to preserve the nutritional and functional characteristics of the crop. Finally, based on the information collected, the potential use of the oils extracted from the fruits of the macauba palm is highlighted in the sense of the elaboration of a new food product, with nutraceutical value and natural appeal.

Keywords: macauba oil, novel food product, quality characteristics

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Valerio PP, Grande SC, Silva AM, Andrade MHC, Cren EC. Evaluating the reduction of acid value in the macaúba mesocarp oil (*Acrocomia aculeata*) from the use of ion exchange resins

Keywords: acid value, physical and physiological factors, *Acrocomia aculeata*

X SLACA – Latin American Symposium of Food Science. Campinas, Brasil. 2013.

Silva AM; Valerio PP; Andrade MHC; Cren EC. 2013. Application and feasibility of ion exchange resins aiming to reduce the acidity level and the carotenoids content of macauba mesocarp oil (*Acrocomia aculeata*)

Keywords: acid value, ion exchange resins, *Acrocomia aculeata*

X SLACA – Latin American Symposium of Food Science. Campinas, Brasil. 2013.

Valério PP, Silva BAP, Caño-Andrade MH, Cren EC. 2013. Physical and physiological factors influencing the acid value of edible vegetable oils mechanically obtained from macauba fruit.

Keywords: Vegetable oils, macauba fruit, physical and physiological factors