UNIVERSIDADE ESTADUAL DO SUDOESTE DA BAHIA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA E CIÊNCIA DOS ALIMENTOS

Área de Concentração: Ciência dos Alimentos

CARACTERIZAÇÃO DO ÓLEO BRUTO DE BABAÇU (*Orbignya phalerata Mart.*) OBTIDO POR DIFERENTES MÉTODOS DE EXTRAÇÃO E SUA APLICAÇÃO NA FORMULAÇÃO DE EMULSÕES DO TIPO ÁGUA EM ÓLEO

ITAPETINGA
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LUCIANA CAROLINA BAUER

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Tese apresentada à Universidade Estadual do Sudoeste da Bahia, como parte das exigências do Programa de Pós-Graduação em Engenharia e Ciência de Alimentos, Área de Concentração em Ciência de Alimentos, Linha de Pesquisa em Química e Bioquímica de Alimentos e Subprodutos.

Orientadora: Profª. Drª. Renata Cristina Ferreira Bonomo

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1. Óleo de babaçu – Aplicação na indústria
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3. Gordura vegetal

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DECLARAÇÃO DE APROVAÇÃO

Título: CARACTERIZAÇÃO DO ÓLEO BRUTO DE BABAÇU (*Orbignya phalerata Mart*.) OBTIDO POR DIFERENTES MÉTODOS DE EXTRAÇÃO E SUA APLICAÇÃO NA FORMULAÇÃO DE EMULSÕES DO TIPO ÁGUA EM ÓLEO.

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Aprovada como parte das exigências para obtenção do Título de ***DOUTORA EM ENGENHARIA E CIÊNCIA DE ALIMENTOS, ÁREA DE CONCENTRAÇÃO: ENGENHARIA DE ALIMENTOS***, pela Banca Examinadora.

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Presidente da Banca

Itapetinga-BA, 03 de março de 2021.

"A verdadeira viagem de descobrimento não consiste em procurar novas paisagens, mas em ter novos olhos".

Marcel Proust

A Deus

À Mariana

Ao Enrico

Ao Otavio

Aos meus pais

Ao meu irmão

Aos meus sonhos

Dedico!

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RESUMO

BAUER, L. C. **Caracterização do óleo bruto de babaçu (*Orbignya phalerata mart.*) obtido por diferentes métodos de extração e sua aplicação na formulação de emulsões do tipo água-em-óleo.** Itapetinga – BA: UESB, 2021. 148 p. (Tese – Doutorado em Engenharia e Ciência dos Alimentos).

Os óleos extraídos dos frutos de palmeiras são os óleos vegetais mais consumidos no mundo, sendo que o principal é o óleo de palma. O dendezeiro não é uma espécie nativa brasileira, porém o país possui grande diversidade de palmeiras potencialmente produtoras de óleos. No Norte e Nordeste do Brasil é bastante difundido entre a população o óleo de babaçu, que é um produto sensorialmente atrativo e de alto valor comercial, porém pouco utilizado pela indústria. Neste contexto, os objetivos desse trabalho foram a caracterização de dois tipos de óleos brutos de babaçu, comumente produzidos, e sua aplicação em um sistema lipídico visando promover sua aplicação em produtos alimentícios. Os óleos estudados foram o óleo de babaçu extra-virgem (EVBO), obtido por prensagem mecânica a frio, e o óleo de babaçu virgem (VBO), obtido por extração a quente. Foram determinados o perfil lipídico, composição em triacilgliceróis, características físico-químicas e propriedades térmicas de ambos os óleos, e ainda, análises térmicas e aquisição dos espectros FTIR de cada um. Além disso, o conteúdo de compostos fenólicos totais e a atividade antioxidante dos óleos foram determinados por meio de ensaios *in vitro*; e, por cromatografia líquida, foi determinado o conteúdo de diferentes compostos bioativos. Os dados obtidos foram submetidos à análise de variância e comparados pelo teste F, análise de regressão e do resíduo ($p < 0,05$). Os resultados mostraram que o óleo de babaçu é uma gordura láurica e o tipo de extração modifica as quantidades de ácidos graxos presentes em cada tipo de óleo. Os principais ácidos graxos presentes são de cadeia média e suas características físico-químicas e propriedades térmicas são essencialmente semelhantes, exceto a estabilidade térmica e a cor, onde o óleo EVBO é mais claro e mais estável que o VBO. Com relação aos compostos bioativos, para maioria dos compostos estudados não houve diferença entre os dois tipos de óleo. Para aqueles em que os óleos diferiam, o VBO apresentou cerca de três vezes o conteúdo do EVBO. Além disso, a atividade antioxidante foi maior para o óleo extraído a quente, estando entre 2,5 vezes até 19,2 vezes maior que a atividade antioxidante do óleo de babaçu extraído por prensagem, demonstrando que o processo de extração pelo calor pode incorporar um número maior de componentes bioativos e melhorar a atividade antioxidante do óleo. Com relação à aplicação, foram formuladas emulsões do tipo água em óleo (20:80 m/m) contendo diferentes quantidades de óleo de babaçu e manteiga de cacau como fase contínua, uma solução de gelatina (20% m/m) como fase dispersa, além da lecitina, como emulsificante. As emulsões foram preparadas pelo método a quente, sendo seis formulações diferentes, contendo desde somente o óleo de babaçu até a completa substituição por manteiga de cacau na fase gordurosa. As emulsões foram caracterizadas quanto as suas propriedades físico-químicas e mecânicas e sua estabilidade em diferentes condições de armazenamento. De acordo com os resultados todas as emulsões mostraram-se estáveis em temperatura amena (≈20°C) ou sob refrigeração. Contudo, a dureza das emulsões diminuiu e a espalhabilidade cinética aumentou à medida que aumentou a quantidade de óleo de babaçu das formulações, o que foi relacionado, principalmente, a cristalização dos lipídios mais amorfa. Assim, como apresentaram diferentes características e boa estabilidade, todas as emulsões demonstraram potencial para aplicação na indústria, seja como ingredientes em diferentes produtos alimentícios ou como bases lipídicas.

Palavras-chave: Gordura vegetal, manteiga de cacau, CG, HPLC, DSC, TGA, DRX, FRAP, DPPH, Compostos fenólicos.

ABSTRACT

BAUER, L. C. **Characterization of babassu crude oil (*Orbignya phalerata Mart*.) obtained by different extraction methods and its application in the formulation of water-in-oil emulsions.** Itapetinga – BA: UESB, 2021. 148 p. (Tese – Doutorado em Engenharia e Ciência dos Alimentos).

Oils extracted from palm fruits are the most consumed vegetable oils in the world, the main one being palm oil. Oil palm is not a native Brazilian species, but the country has a great diversity of palm trees potentially producing oil. In the North and Northeast of Brazil, babassu oil is widespread among the population, which is a sensorially attractive product with high commercial value, but little used by the industry. In this context, the objectives of this work were the characterization of two types of crude babassu oils, commonly produced, and their application in a lipid system in order to promote their application in food products. The oils studied were extra virgin babassu oil (EVBO), obtained by cold mechanical pressing, and virgin babassu oil (VBO), obtained by hot extraction. The lipid profile, composition in triacylglycerols, physicochemical characteristics and thermal properties of both oils were determined, as well as thermal analysis and acquisition of FTIR spectra for each one. In addition, the content of total phenolic compounds and the antioxidant activity of the oils were determined through in vitro tests; and, by liquid chromatography, the content of different bioactive compounds was determined. The data obtained were subjected to analysis of variance and compared using the F test, regression and residue analysis ($p < 0.05$). The results showed that babassu oil is a lauric fat and the type of extraction modifies the amounts of fatty acids present in each type of oil. The main fatty acids present are medium-chain and their physical-chemical characteristics and thermal properties are essentially similar, except for thermal stability and color, where EVBO oil is lighter and more stable than VBO. Regarding bioactive compounds, for most of the compounds studied there was no difference between the two types of oil. For those where the oils differed, the VBO presented about three times the content of the EVBO. In addition, the antioxidant activity was greater for hot extracted oil, being between 2.5 times to 19.2 times greater than the antioxidant activity of babassu oil extracted by pressing, demonstrating that the heat extraction process can incorporate a greater number of bioactive components and improve the antioxidant activity of the oil. Regarding the application, water-in-oil emulsions (20:80 w/w) containing different amounts of babassu oil and cocoa butter were formulated as a continuous phase, a gelatin solution (20% w/w) as a dispersed phase , and lecithin, as an emulsifier. The emulsions were prepared by the hot method, with six different formulations, containing from babassu oil only to the complete substitution by cocoa butter in the fat phase. The emulsions were characterized in terms of their physical-chemical and mechanical properties and their stability under different storage conditions. According to the results, all emulsions were stable at mild temperatures (≈20 °C) or under refrigeration. However, the hardness of the emulsions decreases and the spreadability increases as the amount of babassu oil in the formulations increases, which was mainly related to the crystallization of the more amorphous lipids. Thus, as they have different characteristics and good stability, all emulsions show potential for application in the industry, either as ingredients in different food products or as lipid bases.

Keywords: Vegetable fat, cocoa butter, CG, HPLC, DSC, TGA, DRX, FRAP, DPPH, Phenolic Compounds.

INTRODUÇÃO

Os frutos de palmeiras são uma importante fonte mundial para a produção de óleos vegetais. Segundo o Departamento de Agricultura dos Estados Unidos, em 2020, foram produzidos 87,8 milhões de toneladas dos óleos de palma, palmiste e coco (USDA, 2020), sendo que os maiores produtores estão em regiões de clima tropical, como a Indonésia, Malásia, Tailândia, Colômbia e Nigéria. Além disso, a produção desses óleos cresceu cerca de 29% nos últimos 5 anos, contra um crescimento de apenas 12% dos óleos de oleaginosas, mostrando a importância dos óleos das palmeiras para economia mundial (USDA, 2019).

Atualmente, no Brasil, os óleos provenientes de palmeiras mais utilizados são os óleos de palma e palmiste, sendo que cerca de 80% do total de produção é destinado à indústria alimentícia, para servir de matéria-prima para produtos como margarinas e cremes, sorvetes, biscoitos, chocolates, recheios e substitutos de manteiga de cacau e óleo de cozinha, sendo o restante empregado para fabricação de biocombustíveis, produtos de higiene e limpeza, cosméticos e medicamentos. A palma não é originária do Brasil, foi trazida da África durante o período de escravatura, hoje é na Amazônia que se tem sua maior produção, sendo desenvolvida em larga escala, sobretudo em áreas já desmatadas ou em alto grau de degradação (ABRAPALMA, 2019).

Contudo, pelas suas dimensões e características climáticas, o país tem capacidade para contribuir com fontes endêmicas brasileiras e valorizar sua biodiversidade, já que possui uma grande quantidade de palmeiras potencialmente produtoras de óleo, mas que precisam ser melhor caracterizadas e aproveitadas, como é o caso do babaçu (*Orbignya phalerata Mart.*), que é originário da floresta amazônica da América do Sul, especialmente Brasil, onde é uma das mais importantes palmeiras nativas (SANTOS *et al.*, 2017).

O coco babaçu tem grande valor para o Nordeste brasileiro, especialmente para os estados do Maranhão e Tocantins, que detém quase a totalidade da produção. Isto está relacionado tanto à forma de exploração da cultura, que é essencialmente extrativista e contribui para aumentar a renda dos coletores, como devido à inclusão do óleo e farinha do babaçu na alimentação dessas comunidades, o que melhora o seu aporte nutricional.

O óleo ou azeite de babaçu é o principal produto extraído do babaçueiro, é utilizado habitualmente para cozimento e fritura nas comunidades onde é produzido. Ele é composto por uma grande quantidade de ácidos graxos saturados (80 – 91%), sendo os principais o ácido láurico, o ácido mirístico e o ácido palmítico, e em menor quantidade os ácidos graxos insaturados (9 – 20%), onde estão presentes o ácido oléico e o linoléico (OLIVEIRA *et al.*, 2016; DE OLIVEIRA *et al.*, 2019; SERRA *et al.*, 2019). Esse perfil é semelhante ao do óleo de coco

que já foi relacionado a efeitos benéficos a saúde de quem o consome (NAGAO & YANAGITA, 2010; ALABDUMKARIM *et al.*, 2012; COLEMAN *et al.*, 2016; ZIKER *et al*., 2019) e também ao óleo de palmiste que possui larga utilização na indústria de alimentos, como foi discutido anteriormente. Apesar disso, o óleo de babaçu é quase completamente destinado à indústria cosmética e farmacêutica (GUMIERO & ROCHA FILHO, 2012; AMARAL *et al*., 2014; REIS *et al.*, 2017) ou de biodiesel (DA RÓS *et al.*, 2014; PAIVA *et al*., 2013), sendo baixo o seu emprego na indústria de alimentos, o que pode estar relacionado à excassez de dados a respeito das suas características importantes para este setor industrial.

A literatura sobre o óleo de babaçu está limitada a sua composição química em ácidos graxos e outros componentes lipídicos, dados sobre processos e redimento de extração do óleo das suas amêndoas e alguns parâmetros, como acidez, índice de saponificação, índice de refração e densidade a 25°C (OLIVEIRA *et al.*, 2016; DE OLIVEIRA *et al*., 2019; SERRA *et al*., 2019), contudo apenas esses dados não são suficientes para uma aplicação mais assertiva. Portanto, para que uma matéria-prima seja adequadamente utilizada na indústria, especialmente de alimentos, outras características precisam ser avaliadas, como as propriedades térmicas, físicas, sensoriais e nutritivas, pois são elas que vão determinar o comportamento daquele material dentro do alimento (que é um sistema complexo), sua funcionalidade, as condições adequadas de processamento e armazenagem, bem como a aceitabilidade perante os consumidores.

Diante do exposto, fica evidenciada a necessidade de desenvolver pesquisas sobre novas fontes de matérias-primas voltadas para a indústria de alimentos, que possam associar propriedades funcionais adequadas aos processos e produtos alimentícios, aumentando o valor agregado a esses alimentos, e que tenham potencial para oferecer benefícios nutricionais aos consumidores. Dessa forma, este trabalho de pesquisa teve como objetivo promover a utilização do óleo de babaçu na fabricação de alimentos, por meio da caracterização química, física e térmica dos óleos brutos de babaçu, obtidos por diferentes métodos de extração, e sua aplicação na formulação de um sistema lipídico (emulsão A/O) que possa ser utilizado como ingrediente para a indústria.

Esta pesquisa foi estruturada em seis capítulos que estão divididos da seguinte forma:

I. Capítulo1 – Revisão Bibliográfica: delineia a importância dos óleos vegetais para a indústria de alimentos, especialmente daqueles oriundos de frutos de palmeiras, suas características e aplicação industrial. Apresenta os dados e informações difundidas sobre o babaçu e o óleo extraído de suas amêndoas, suas propriedades e as análises que ainda são necessárias para uma caracterização mais completa e que possibilite a sua utilização na produção de alimentos, seja diretamente na formulação do produto ou como ingrediente de cremes vegetais especiais;

II. Capítulo 2 – Objetivos: expõe os objetivos, geral e específicos, que nortearam as etapas da pesquisa e permitiram as pressuposições do trabalho;

III. Capítulo 3 – Artigo 1: descreve a caracterização química, física e térmica dos óleos brutos de babaçu e as diferenças entre suas características que são resultantes, principalmente, do tipo de processo utilizado para sua obtenção. O primeiro, denominado de óleo de babaçu virgem (VBO) que foi extraído por meio do cozimento da massa de amêndoas do coco babaçu, e o segundo, denominado óleo de babaçu extra-virgem (EVBO), obtido por prensagem mecânica das amêndoas, ou seja, um extraído com uso de calor e o outro a frio;

IV. Capítulo 4 – Artigo 2: descreve as etapas da investigação sobre a atividade antioxidante dos dois tipos de óleo de babaçu estudados, VBO e EVBO, e de que forma o tipo de extração é capaz ou não de influenciar nessa atividade;

V. Capítulo 5 – Artigo 3: apresenta o processo de elaboração e caracterização de emulsões do tipo água em óleo contendo diferentes quantidades de óleo de babaçu e manteiga de cacau na composição da fase contínua, desde a totalidade de óleo de babaçu até sua completa substituição por manteiga de cacau;

VI. Capítulo 6 – Considerações Finais: por fim, este capítulo traz as principais conclusões deste estudo e as implicações futuras desta pesquisa.

Capítulo 1

Revisão Bibliográfica

1 REVISÃO BIBLIOGRÁFICA

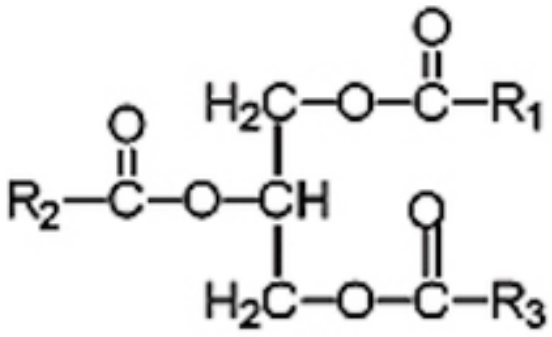
1.1 Óleos e Gorduras

1.1.1 Composição

Os óleos e gorduras comestíveis podem ser extraídos tanto de fontes animais quanto vegetais e compreendem a maior parte da classe dos lipídios. Os termos “óleo” e “gordura” são utilizados para representar o estado físico do material à temperatura ambiente (25°C) (MARANGONI & WESDORP, 2013), sendo óleo utilizado para líquidos, por exemplo, óleo de soja; e gordura utilizado para semissólidos, como a gordura animal e algumas de origem vegetal, como a manteiga de cacau.

Quimicamente, óleos e gorduras são compostos majoritariamente por triacilgliceróis (96 – 99%) (INDELICATO *et al*., 2017), que são estruturas formadas por três moléculas de ácidos graxos esterificados com uma molécula de glicerol (Figura 1). Em pequenas quantidades, óleos e gorduras também contêm ácidos graxos livres, monoacilgliceróis, diacilgliceróis e outros compostos como esteróis, fosfolipídios, vitaminas lipossolúveis, pigmentos e minerais (DIJKSTRA, 2016; SAVVA & KAFATOS, 2016).

Figura 1. Estrutura química de um triacilglicerol. R_1, R_2 e R_3 representam moléculas de ácidos graxos.



Fonte: Adaptado de Química E Sociedade (2016).

Com relação aos ácidos graxos, estes podem ser diferenciados de acordo com o tamanho de sua cadeia carbônica, grau de saturação e tipo de isomeria, *cis* ou *trans*. Dependendo do tamanho de sua cadeia carbônica podem ser considerados de cadeia curta (até 6 carbonos), cadeia média (entre 6 e 12 carbonos) e cadeia longa (mais que 14 carbonos). Quando possuem

apenas ligações carbônicas simples são saturados, quando possuem uma ligação dupla são monoinsaturados, e quando possuem duas ou mais ligações carbônicas duplas são poliinsaturados (McCLEMENTS & DECKER, 2007). Os principais ácidos graxos encontrados em alimentos possuem cadeias carbônicas com número par de carbonos e estão apresentados na Tabela 1.

Tabela 1. Ácidos graxos encontrados em alimentos, cadeia carbônica e isomeria.

Ácido Graxo	Abreviação	Abreviação Numérica	Isomeria
Butírico	B	4:0	-
Capróico	Co	6:0	-
Caprílico	Ci	8:0	-
Cáprico	C	10:0	-
Láurico	La	12:0	-
Mirístico	M	14:0	-
Palmítico	P	16:0	-
Palmitoléico	Po	16:1	*Cis*
Esteárico	St	18:0	-
Oléico	O	18:1	*Cis*
Linoléico	L	18:2	*Cis*
Linolênico	Ln	18:3	*Cis*
Araquídico	Ar	20:0	-
Araquidônico	AA	20:4	*Cis*
EPA	EPA	20:5	*Cis*
DHA	DHA	22:6	*Cis*

Fonte: Adaptado de McClements e Decker (2007) e O'Brien (2004).

Os triacilgliceróis podem receber diferentes classificações. São classificados como monoácidos, quando os três ácidos graxos ligados à molécula de glicerol são iguais, em diácidos e triácidos, quando possuem dois e três tipos de ácidos graxos diferentes, respectivamente. Ainda podem, segundo o grau de saturação de seus componentes, ser trissaturados, que contém somente ácidos graxos saturados, dissaturados ou monossaturados, que cotém duas ou uma cadeia saturada e triinsaturados, que possuem três ácidos graxos insaturados ligados ao glicerol. E por último, ainda podem ser simétricos ou assimétricos, quando possuem ácidos graxos com cadeia carbônica de tamanhos equivalentes ou não, respectivamente (McCLEMENTS & DECKER, 2007; GUNSTONE, 2011).

Como os ácidos graxos podem se ligar em qualquer uma das posições da molécula de glicerol (R_1, R_2 e R_3, Figura 1) existe uma série de combinações possíveis para os triacilgliceróis (INDELICATO *et al.*, 2017), e que, consequentemente, influenciam as propriedades físicas dos produtos com base lipídica, especialmente brilho, dureza/maciez, fusão, textura e palatabilidade (MARANGONI *et al*., 2012; MARANGONI & WESDORP, 2013; BAYÉS-GARCIA *et al*., 2015).

1.1.2 Babaçu

O babaçu (*Orbignya phalerata Mart.*) (Figura 2a) é uma palmeira endêmica da floresta amazônica da América do Sul, especialmente Bolívia, Peru, Colômbia e Brasil (SANTOS *et al*., 2017). É comumente encontrada nas regiões brasileiras do Norte e Nordeste em formações denominadas babaçuais e que estão concentradas nos estados do Maranhão, Tocantins e Piauí. Essa palmeira pode alcançar entre 10 a 30 metros de altura e apresenta entre três a cinco cachos que produzem de 250 a 500 cocos cada, sendo o período de amadurecimento dos frutos entre agosto e dezembro (LORENZI, 2010; SANTOS *et al*., 2017).

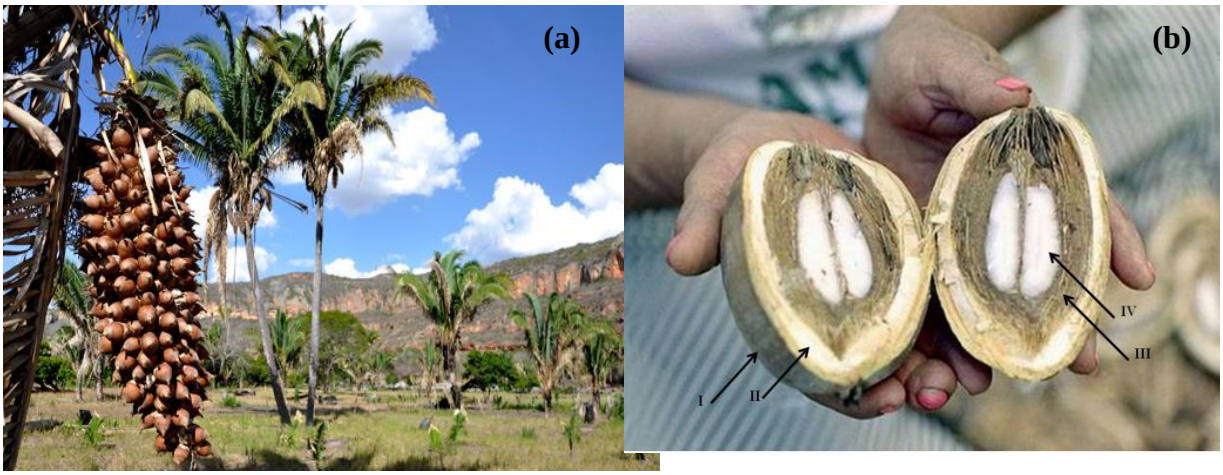
Os produtos derivados do babaçu, como seus frutos ou cocos, folhas e extratos são utilizados há muitas gerações como parte da medicina popular, no tratamento de problemas estomacais, feridas cutâneas, inflamações diversas e cólicas menstruais (SOUZA *et al*., 2011; AGOSTINI-COSTA, 2018; MAGALHÃES *et al.*, 2019) sendo atribuído a ele efeitos antiinflamatórios (REIS *et al.*, 2017), analgésicos (PINHEIRO *et al*., 2012), antioxidantes (NOBRE *et al.*, 2018a), antimicrobianos e imunomoduladores (BARROQUEIRO *et al*., 2016; NOBRE *et al*., 2018).

Os cocos são frutos lenhosos, em formato de drupas, com peso entre 90 a 280 g, tem anatomia diferente dos frutos de outros tipos de palmas, sendo formados por epicarpo (12,6%), mesocarpo (20,4%), endocarpo (58,4%) e amêndoas (8,6%) (Figura 2b). O epicarpo é uma camada fina, rija e fibrosa; o mesocarpo possui entre 0,5 a 1,0 cm de espessura e é rico em amido; o endocarpo é a camada mais resistente, possui entre 2 a 3 cm de espessura, tem aspecto semelhante às madeiras duras; e, por fim, as amêndoas, que são em média de 2 a 5 unidades por coco, ficam na parte central do fruto e são a parte de maior valor econômico (TEIXEIRA, 2008; LORENZI, 2010; CARRAZZA *et al*., 2012).

O coco babaçu é o principal produto do babaçueiro e é considerado um recurso importante tanto em termos econômicos quanto nutricionais. Segundo dados sobre a Produção da Extração Vegetal e Silvicultura levantados pelo Instituto Brasileiro de Geografia e Estatística (IBGE, 2019) a amêndoa do babaçu foi o terceiro produto não madeireiro e alimentício mais

extraído no país, alcançando produção de 48.706 toneladas e movimentando cerca de R$ 89,4 milhões, sendo que somente a região Nordeste concentrou 98,97% desse total, com destaque para o estado do Maranhão, maior produtor nacional. Essa importância está relacionada tanto à forma de exploração da cultura, como ao grande número de produtos e subprodutos que podem ser originados através do aproveitamento integral do coco.

Figura 2. No primeiro plano cacho de babaçu, no segundo, palmeiras da espécie no babaçual (a). Coco babaçu (b): epicarpo (I); mesocarpo (II); endocarpo (III); e amêndoas (IV).



Fonte: CERRATINGA (2017).

Apesar de nas regiões de produção se plantar e manejar a palmeira do babaçu, ainda não existe o plantio sistematizado de babaçuais, sendo que as tentativas de se organizar o manejo fracassaram devido ao fato da exploração extrativista estar muito presente nas comunidades que vivem dessa cultura (TEIXEIRA, 2008). A quebra do coco é feita principalmente por mulheres conhecidas como quebradeiras, que utilizam um machado e um porrete de madeira para abrir o fruto e separar as amêndoas que são vendidas para a indústria ou processadas de forma artesanal (CARRAZZA *et al*., 2012).

O óleo ou azeite de babaçu é o principal produto, utilizado habitualmente na dieta dessas comunidades ou para produção de cosméticos e produtos de higiene e limpeza, sendo os subprodutos destinados a outros usos, como o aproveitamento do mesocarpo para produção de farinha, aproveitamento da torta de extração para alimentação animal e a utilização das cascas para produção de carvão vegetal ou queima em fornos e fogueiras e confecção de artesanatos, entre outros (TEIXEIRA, 2008; ALBUQUERQUE *et al*., 2009; CARRAZZA *et al*., 2012; FONSECA *et al*., 2014).

Pesquisas recentes tem demonstrado as potencialidades e a diversidade de usos do babaçu em diferentes segmentos, na indústria de alimentos e biofilmes (MANIGLIA & TÁPIA-

BLÁCIDO, 2016; MANIGLIA *et al*., 2017; LEAL *et al*., 2018; DA SILVA *et al*., 2019; MANIGLIA *et al*., 2019), indústria médica, farmacêutica e cosmética (DO AMARAL *et al*., 2014; BARROQUEIRO *et al*., 2016; SCHEIBE *et al*.; 2016; REIS *et al*., 2017; NOBRE *et al*., 2018), biodisel e energia (DA RÓS *et al*., 2014; AGUIEIRAS *et al*., 2017; RANUCCI *et al*., 2018) e química e ambiental (HOPPEN *et al*., 2019; GHOSH *et al*., 2019).

1.1.2.1 Óleo de Babaçu

A maior parte da amêndoa de babaçu é composta de óleo, aproximadamente 65% (ALBIERO *et al*., 2007), e seu processamento é basicamente realizado de forma doméstica ou por cooperativas (CARRAZZA *et al*., 2012). Este óleo é geralmente empregado na culinária ou fabricação dos produtos de venda direta nas comunidades e comércio regional ou repassado para a indústria, onde é refinado e utilizado na fabricação de produtos de limpeza, higiene ou cuidados pessoais.

Segundo Carrazza *et al*. (2012), o óleo bruto de babaçu é obtido por processos de extração mecânica à frio com ou sem aplicação de cozimento posterior. Na prensagem a frio, após a coleta e quebra dos cocos, as amêndoas de babaçu são selecionadas, separando-se apenas aquelas inteiras, sadias, sem coloração amarelada ou danos físicos superficiais, que são então trituradas e prensadas em prensa hidráulica para obtenção do óleo, que é filtrado e envasado e denominado extra-virgem.

No processo para obtenção do óleo de babaçu virgem, após a seleção, as amêndoas são picadas grosseiramente e torradas para posterior trituração fina. A farinha triturada é cozida com um pouco de água para desprendimento do óleo, que por ser menos denso sobrenada sobre a torta úmida e pode ser separado com o auxílio de uma concha ou por filtração/decantação. Neste caso, o óleo coletado possui certa quantidade de água sendo necessária uma nova etapa de aquecimento para evaporação dela e obtenção do óleo, que é então envasado (CARRAZZA *et al*., 2012).

O óleo industrial de babaçu é obtido através do refino do óleo bruto extraído de forma artesanal ou pela extração do óleo das amêndoas por solventes e posterior etapa de refino (CARVALHO, 2007). A refinagem mais empregada é a clássica para óleos e gorduras, que segue três etapas, a neutralização, a clarificação e a desodorização, sendo que o óleo refinado apresenta concentração mais elevada de triglicerídeos, coloração, sabor e odor neutros (DE GREYT, 2013).

Independente do processo de extração, o óleo de babaçu é composto majoritariamente por ácidos graxos saturados (80 – 91%), sendo estes, ácido láurico (43 – 50%), ácido mirístico (15 –

18%), ácido palmítico (6 – 10%), ácido cáprico (4 – 6%), ácido caprílico (0 – 5%) e ácido esteárico (3– 5%); o restante são ácidos graxos insaturados (9 – 20%), onde estão presentes o ácido oléico (12 – 19%) e o linoléico (1 – 3%) (OLIVEIRA *et al.*, 2016; DE OLIVEIRA *et al*., 2019; SERRA *et al*., 2019).

O óleo de babaçu possui alto valor agregado e muitas vezes é considerado um óleo especial para indústria, seu perfil lipídico é característico do grupo denominado de gorduras láuricas, que são óleos ou gorduras cujo principal componente é o ácido láurico, mas também possuem quantidades significativas dos ácidos caprílico, cáprico e mirístico (Tabela 2). Dentre as principais características das gorduras láuricas estão a resistência à oxidação não enzimática; o ponto de fusão mais baixo e bem definido (≈ 25°C), quando comparado a outras gorduras saturadas e a capacidade surfactante dos seus componentes, principalmente triacilgliceróis com menor número de carbonos (30-38) (DIJKSTRA, 2016). Além disso, o óleo de babaçu pode ser apontado como a principal fonte alternativa para o mercado dos óleos de palmiste e coco, isso devido ao seu perfil lipídico e características físicas semelhantes e capacidade para volume de produção (GUEDES *et al*., 2015; DE OLIVEIRA *et al*., 2016; DIJKSTRA, 2016), podendo ser empregado na fabricação de produtos alimentícios como sorvetes, biscoitos, chocolates, recheios e substitutos de manteiga de cacau, óleo para cozimento e fritura ou base para gorduras e cremes especiais, e ainda, nas indústrias química, farmacêutica e cosmética.

Tabela 2. Composição (%) em ácidos graxos das principais gorduras láuricas: palmiste, coco, babaçu e licuri.

Ácido Graxo	Palmiste[a]	Coco[a]	Babaçu[b]	Licuri[c]
Capróico	0,20	0,40	-	0,35
Caprílico	3.30	7.30	8,57	9,61
Cáprico	3,50	6,60	7,42	6,29
Láurico	47,80	47,80	49,97	44.20
Mirístico	16,30	18,10	14,22	14,45
Palmítico	8,50	8,90	6,59	6,92
Esteárico	2,40	2,70	2,69	3,08
Oléico	15,40	6,40	8,98	12,08
Linoléico	2,50	1,60	1,52	2,79

Fonte: [a](DIJKSTRA, 2016); [b](SERRA *et al*., 2019); [c](BAUER *et al*., 2013).

O óleo de babaçu pode ser considerado fonte de ácidos graxos de cadeia média (6 a 12 átomos de carbono na cadeia acila) que são considerados lipídios funcionais quando consumidos em quantidades moderadas e estão relacionados a efeitos benéficos à saúde (ALABDUMKARIM *et al*., 2012). Entre os principais benefícios estão a prevenção e o tratamento da obesidade, por meio do aumento da termogênese, oxidação da gordura e gasto de energia (NAGAO & YANAGITA, 2010; ZIKER *et al*., 2019), aumento da saciedade e diminuição da ingestão de alimentos (COLEMAN *et al*., 2016) e propriedades antidiabéticas (NAGAO & YANAGITA, 2010; ZIKER *et al*., 2019; NUNES *et al*., 2020).

Além disso, outros benefícios fisiológicos constituem outras vantagens do uso ou ingestão do óleo de babaçu, como efeitos antimicrobianos, efeitos imunomoduladores e melhora de sintomas clínicos, principalmente aqueles ligados a doenças como o câncer (AMARAL *et al.*, 2014; RIAL *et al.*, 2016; PEREIRA *et al.*, 2020). Estes benefícios geralmente são atribuídos a sua composição em ácidos graxos, principalmente a grande quantidade de ácido láurico que possui essas propriedades terapêuticas (DAYRIT, 2015; LAPPANO *et al*., 2017) e também a presença dos ácidos insaturados como o oleico e linoleico (PEREIRA *et al*., 2020).

1.1.3 Caracterização Química e Física dos Óleos e Gorduras

Assim, como para outros materiais, um conjunto de análises básicas deve ser realizado para a caracterização de óleos e gorduras. Essas normas foram descritas pela Organização das Nações Unidas para Alimentação e Agricultura (FAO) e também pela Organização Mundial da Saúde (OMS) e são aceitas internacionalmente pela maioria dos países, inclusive o Brasil. No país, o órgão responsável pela regulamentação e parâmetros de qualidade exigidos para óleos e gorduras de origem vegetal é a Agência Nacional de Vigilância Sanitária (ANVISA) que é vinculada ao Ministério da Saúde. Através da Resolução-RDC Nº 270, de 22 de setembro de 2005, a agência descreve o "Regulamento técnico para óleos vegetais, gorduras vegetais e creme vegetal" descrevendo os requisitos específicos e de composição para cada tipo de óleo e/ou gordura (BRASIL, 2005).

A Norma para Óleos Vegetais Especificados (Codex Stan 210-1999) (ALIMENTARIUS, 2015), que é a norma que fundamenta a legislação brasileira, prevê como caracterização básica a composição em ácidos graxos e parâmetros de qualidade, que compreendem a matéria volátil, impurezas insolúveis e os índices de saponificação, acidez e de peróxidos. Além das medidas físicas da densidade a 25°C e do índice de refração a 40°C. Essas técnicas são consideradas clássicas e amplamente conhecidas e estão descritas em manuais de métodos de análise como os

publicados pela Organização Internacional pela Padronização (ISO) e pela Sociedade Americana de Química de Óleos (AOCS).

Entretanto, para que uma matéria-prima seja adequadamente utilizada é necessário que se tenha conhecimento mais amplo a respeito de suas características, sua composição química e seu comportamento físico, em especial na indústria de alimentos que envolve a mistura complexa de diferentes ingredientes que incluem a presença de antioxidantes e pró-oxidantes, variações na temperatura e pH, e períodos relativamente longos de armazenamento (FENEMA *et al.,* 2010). Assim, à medida que novas técnicas de análise foram sendo desenvolvidas novas características puderam ser compreendidas.

Atualmente, os trabalhos publicados envolvem a caracterização mais aprofundada dos óleos e gorduras, em particular para novas matérias-primas ou misturas lipídicas substitutas, como a investigação de componentes nutricionalmente funcionais (FLAKELAR *et al.*, 2015; KOZLOWSKA *et al.*, 2016; KUA *et al.*, 2016; FLAKELAR *et al.*, 2017), composição em triacilgliceróis (SPERANZA *et al.*, 2016; TIMILSENA *et al.*, 2017; LIU *et al.*, 2018; PEREIRA *et al.*, 2019; LIEB *et al.*, 2019), polimorfismo (HERNÁNDEZ-SANTOS *et al.,* 2017; LIU *et al.*, 2018; CHAI *et al.,* 2018) e comportamento de cristalização e fusão (HERNÁNDEZ-SANTOS *et al.,* 2017; TIMILSENA *et al.,* 2017; HUBBES *et al.,* 2018; LIU *et al.,* 2018; PEREIRA *et al.,* 2019; LIEB *et al.,* 2019). Esses parâmetros são determinantes para aplicação ou não de determinado lipídio em um produto específico.

Entre os principais compostos nutracêuticos, os compostos bioativos como os antioxidantes naturais e vitaminas lipossolúveis são os mais pesquisados, como por exemplos compostos fenólicos, carotenos e tocoferóis. Comumente a combinação de testes qualitativos para a capacidade antioxidante seguida da identificação dos compostos específicos são as técnicas utilizadas (FRANCO *et al.*, 2014; KOZLOWSKA *et al.,* 2016; BAUER *et al.*, 2019).

Os principais ensaios para a determinação da capacidade antioxidante são baseados em dois mecanismos de reação, a capacidade de transferência de um átomo de hidrogênio e/ou de transferência de um elétron. Além do mecanismo, o objetivo é determinar o efeito protetor do material contra os radicais livres, que diferem no radical iniciador, na cinética da reação e nas reações colaterais (APAK *et al.,* 2016), esses métodos são todos espectrofotométricos e os mais utilizados são: para capacidade antioxidante total, Folin-Ciocauteal e ensaios de capacidade de sequestro dos radicais peroxil ou de oxigênio (TRAP e ORAC), sequestro de outros radicais (DPPH ou ABTS) e poder redutor de metais pró-oxidantes, como ferro ou cobre (FRAP ou CUPRAC).

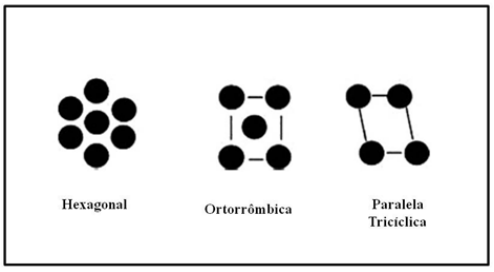
Com relação à identificação dos compostos bioativos e vitaminas a técnica mais empregada é a separação por cromatografia líquida de alta eficiência acoplada a diferentes

detectores, como o arranjo de diodos (KUA *et al.,* 2016; FLAKELAR *et al.,* 2017; SERRA *et al.,* 2019; BAUER *et al.,* 2019) e fluorescência (FLAKELAR *et al.,* 2015; SERRA *et al.,* 2019; BAUER *et al.,* 2019).

As análises sobre a composição em acilgliceróis têm sido realizadas, pois é ela, principalmente, que determina as propriedades químicas, físicas e de textura dos óleos e gorduras. Geralmente duas técnicas são utilizadas, a cromatografia gasosa e a líquida de alta eficiência. A primeira para determinar o perfil de ácidos graxos e as proporções em tri, di e monoacilgliceróis dos óleos (PEREIRA *et al.,* 2019) e a segunda para identificação e quantificação dos triacilgliceróis específicos de cada amostra (KOSEOGLU *et al.,* 2016). Outros trabalhos ainda tem usado a combinação entre as informações do conteúdo em triacilgliceróis e o perfil de ácidos graxos para predizer a composição em triglicerói̇s de cada óleo ou gordura (PEREIRA *et al.,* 2019; DE OLIVEIRA *et al.,* 2019).

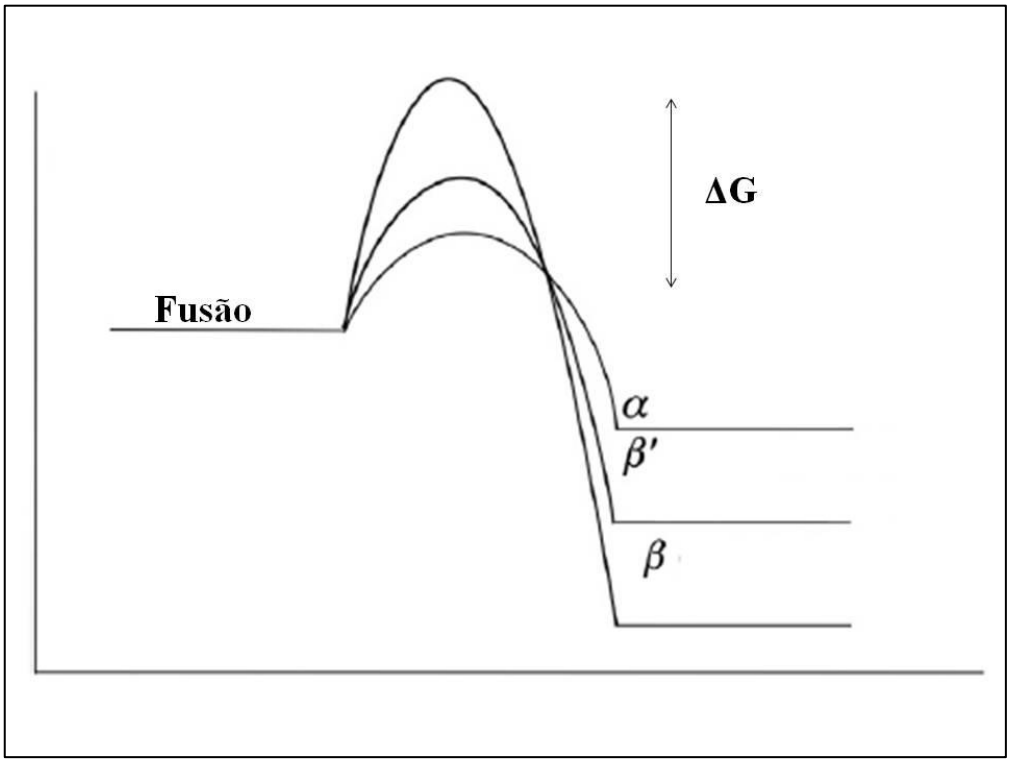
Polimorfismo é definido como a capacidade de um composto químico para formar estruturas cristalinas diferentes, sendo que três formas, α, β′ e β são as formas polimórficas típicas das gorduras e podem ocorrer concomitantemente em um determinado óleo ou gordura (DOUAIRE *et al.,* 2014). Os polimorfos são definidos pelo tipo de empacotamento nas suas sub-células, hexagonal, ortorrômbica e paralela tricíclica (Figura 3), além do tamanho das cadeias acila dos ácidos graxos e da conformação da molécula do glicerol (SATO & UENO, 2011; MARANGONI & WESDORP, 2013; BAYÉS-GARCIA *et al.*, 2015; ROGERS, 2017). Dessa forma, cada tipo de triacilglicerol assume uma estrutura e tem um comportamento de cristalização e fusão distinto, com a estabilidade crescente de α < β′ < β (Figura 4) (ROGERS, 2017). Gorduras capazes de se organizar como polimorfo β′, a forma metaestável, são usadas na fabricação de margarina e cremes vegetais, por causa da sua morfologia que da origem à textura macia desses produtos, por outro lado, o polimorfo do tipo β é encontrado em gorduras de confeitaria feitas a partir da manteiga de cacau e chocolates, ele é mais duro e é responsável pelo *snap* característico no chocolate (SATO & UENO, 2011).

Figura 3. Ilustração das estruturas polimórficas das gorduras, α (hexagonal), β’ (ortorrômbica) e β (paralela tricíclica).



Fonte: Adaptado de Rogers (2017).

Figura 4. Energias de ativação e estabilidade termodinâmica dos três principais polimórficos presentes nas gorduras.



Fonte: Adaptado de Rogers (2017).

A identificação do tipo de polimorfismo de um lipídio comumente é realizada por difração de raios-X, através da qual é possível determinar as distâncias entre os grupos alquilas paralelos dos triacilgliceróis. Geralmente utilizam-se ângulos de incidência entre 10° a 30° e as distâncias entre os cristais lipídicos são denominadas como espaçamentos curtos ou *short spacings* (SS). O princípio da técnica obedece a Lei de Bragg, em que a relação entre o ângulo incidente 'θ' (°) e a distância entre os planos refletidos 'd' (Å), dependem do comprimento de onda 'λ', que geralmente corresponde a 1,54 Å (Equação 1), considerando as fontes de radiação CuKα, mais utilizada por ser de fácil acesso e mais viável economicamente (SKOOG *et al.*, 2002). As distâncias comuns para os polimorfos dos lipídios são para a forma α (d = 4.15 Å), para a forma β' (d = 3.8 e 4.2 Å) e para a forma β (d = 4.6 Å), e mudanças neste perfil de difração (seja alteração na forma ou posição do pico) indica uma mudança no polimorfismo ou presença de polimorfos metaestáveis como β'_1 e β'_2 (MARANGONI & WESDORP, 2013; ROGERS, 2017).

$$d = \frac{n\lambda}{2 \sin \theta} \quad (1)$$

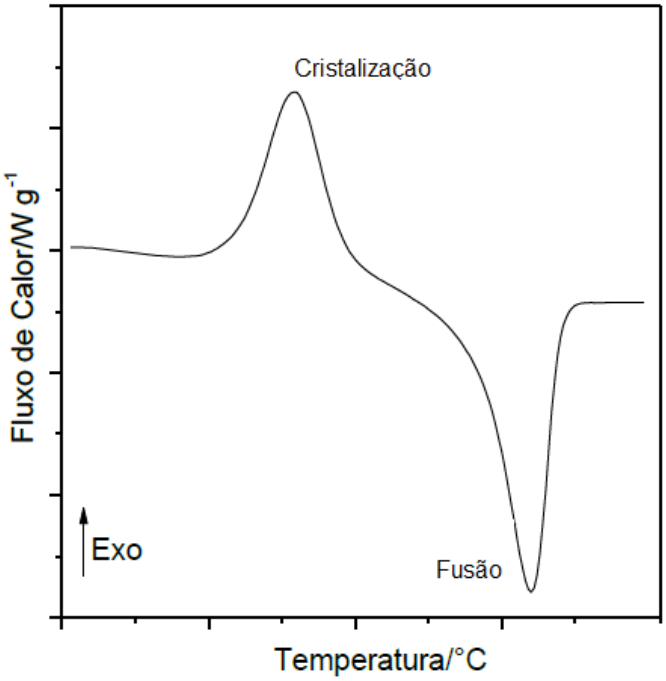
Onde: d é a distância interplanar entre as cadeias de triacilgliceróis; n é o tipo de interferência construtiva e geralmente equivale a 1; λ é o comprimento de onda dos raios-X; e θ é o ângulo de incidência no pico registrado no difratograma.

A cristalização e a fusão das gorduras não ocorrem em uma temperatura específica. Como são misturas de ácidos graxos e triglicerídeos, o comportamento é definido pelas proporções de cada componente e representado por uma faixa de temperatura (TAN & CHE MAN, 2000), além de também ser influenciado pelo tipo de polimorfo formado (ROGERS, 2017). O processo de nucleação e cristalização inicia quando o lipídio líquido é resfriado a uma temperatura cerca de 5°C abaixo do ponto de fusão do seu triacilglicerol de maior ponto de fusão e vai até que todo material (óleo ou gordura) esteja no estado sólido (TRAN & ROUSSEAU, 2016). O mesmo acontece na fusão, porém, ela inicia quando a temperatura do material atinge valores semelhantes à temperatura de mudança de fase do seu triacilglicerol com menor ponto de fusão (MARANGONI & WESDORP, 2013).

Diferentes óleos vegetais mostram perfis térmicos complexos e que se devem principalmente à variedade nos constituintes (TAN & CHE MAN, 2000) e mesmo para gorduras de uma mesma fonte, o perfil térmico pode ser influenciado por pequenas variações nesses constituintes, conforme demonstraram Lieb *et al.* (2019) e Chai *et al.* (2018). Além da composição, outros fatores como taxa de troca de calor (TAN & CHEN, 2002) e cisalhamento (TRAN & ROUSSEAU, 2016) podem influenciar no comportamento térmico dos óleos e gorduras, porém para efeito de caracterização, comumente só a tranferência de calor é investigada.

O comportamento térmico dos óleos e gorduras é determinado por meio da calorimetria exploratória diferencial ou DSC, sigla em inglês para, *Differential Scanning Calorimetric*, que é uma técnica baseada na medição da diferença das energias fornecidas a uma amostra e uma substância de referência, em função da temperatura, quando ambas são submetidas a um programa controlado de temperatura, resfriamento ou aquecimento (SKOOG *et al.*, 2002). A absorção de calor durante um experimento DSC é registrada como um pico endotérmico, denominado pico de fusão, e a liberação de energia é registrada como pico exotérmico, pico de cristalização (Figura 5). Dessa forma é possível obter as medidas das temperaturas inicial, máxima e final da transição de fase e calcular o calor ou entalpia (J/g) necessário para fundir ou cristalizar um óleo ou gordura, que é determinado pelo cálculo da área sob o pico no termograma (THOMAS & SCHMIDT, 2017).

Figura 5. Termograma ilustrativo para análise DSC de um material.



(Fonte: Adaptado de Denari & Cavalheiro, 2012).

1.1.4 Óleos e Gorduras na Indústria de Alimentos

As principais fontes lipídicas industriais são os óleos e gorduras vegetais, como por exemplo, de sementes oleaginosas, como a soja, a canola e o amendoim, e de frutos, como dendê, cacau e azeitona. As fontes vegetais são vantajosas porque podem ser cultivadas de acordo com a demanda do mercado, sendo que, atualmente, os óleos mais produzidos e consumidos mundialmente são o óleo de palma (75,45 milhões de toneladas), soja (60,27 milhões de toneladas), canola (27,64 milhões de toneladas), girassol (19,27 milhões de toneladas) e palmiste (8,77 milhões de toneladas), sendo os maiores produtores a Indonésia, a China, a Malásia e a União Européia (USDA, 2020).

Esses óleos se destacam pela facilidade de cultivo agronômico, alto rendimento na extração dos óleos e desenvolvimento nas tecnologias de processamento e manipulação dos lipídios, como extração, refino, fracionamento, hidrogenação, interesterificação e misturas para novas bases lipídicas. Além desses, a manteiga de cacau é uma gordura vegetal que também merece destaque, ela possui características únicas o que a torna uma matéria-prima de alto valor agregado e aplicação quase exclusiva a um produto, o chocolate (BEG *et al*., 2017).

Os óleos oriundos dos frutos de palmeiras apresentam características únicas, como por exemplo, composição equivalente em ácidos graxos saturados e insaturados (1:1) (MBA *et al*., 2015) e altos teores de compostos antioxidantes no óleo de palma (MBA *et al*., 2015; SAMPAIO

et al., 2017) e grande quantidade de ácido láurico (≥50%) nos óleos de palmiste, coco, babaçu, licuri, tucum, entre outros (DIJKSTRA, 2016). Através do seu fracionamento a indústria produz bases lipídicas especiais naturais, como oleínas, estearinas e frações médias de palma (MBA *et al*., 2015; HARWOOD *et al*., 2017), e gorduras com altos teores de ácido láurico, com alto valor comercial, usados na produção de tensoativos de grau alimentício, substitutos da manteiga de cacau, recheios cremosos e sorvetes (HARWOOD *et al*., 2017). O fracionamento é um processo no qual algumas gorduras e óleos são separados em duas ou mais frações com diferentes propriedades de fusão e textura, esse processo exige o resfriamento dos lipídios e controle na cristalização, dessa forma tem custo relativamente elevado (DE GREYT *et al.*, 2013; MBA *et al.*, 2015).

Os óleos das sementes oleaginosas são óleos ricos em ácidos graxos poliinsaturados e fonte de ácidos graxos essenciais, como linolênico (ω-3) (SAVVA & KAFATOS, 2016). Eles são líquidos a temperatura ambiente e são os óleos mais transformados na indústria química e de alimentos (HASHEMPOUR-BALTORK *et al*., 2016), principalmente para produzir diferentes bases lipídicas com diferentes quantidades de gorduras sólidas, o que fornece uma gama grande de produtos com diferentes propriedades físicas de consistência e textura, indo do líquido até o sólido (MARTIN *et al*., 2007). Os processos mais utilizados nestes casos são a hidrogenação e a interesterificação.

A hidrogenação de óleos vegetais para obter óleos ou gorduras com melhor textura e estabilidade oxidativa tem sido usada há muito tempo, inserindo moléculas de hidrogênio para saturar algumas ou todas as duplas ligações nos ácidos graxos insaturados. Durante esse processo, algumas ligações duplas podem ser isomerizadas e convertidas do estado *cis* para o estado *trans* que tem efeitos negativos na saúde e podem causar doenças, principalmente cardiovasculares (IQBAL, 2014; SHAH & THADANI, 2019). A interesterificação é um processo alternativo à hidrogenação, onde os ácidos graxos são redistribuídos na estrutura do triacilglicerol sem que haja saturação ou isomerização, entretanto, esse processo precisa de equipamentos especiais e é o mais caro (DIJKSTRA, 2015). Dessa forma, atualmente a indústria tem priorizado a mistura dos óleos e gorduras para produção de novos produtos, produzidos a base de frações de gorduras de espécies de palmeiras e óleos de sementes oleaginosas (HASHEMPOUR-BALTORK *et al.*, 2016), ou ainda a busca por outras fontes, consideradas não convencionais e que tragam características distintas (GUNSTONE, 2011; TALBOT, 2015; HARWOOD *et al.*, 2017).

A manteiga de cacau é um dos principais ingredientes do chocolate e está presente em uma variedade de produtos, como bebidas cremosas, sorvetes e produtos de panificação e confeitaria, ela confere um sabor característico e único aos seus produtos derivados. A manteiga

de cacau é composta basicamente por três ácidos graxos com cadeias de tamanho semelhantes o que reflete em suas características especiais de textura, que são os ácidos oleico (35%), esteárico (34%) e palmítico (26%) (AFOAKWA *et al.*, 2007). Segundo Beg *et al.* (2017), a demanda mundial por cacau e derivados deverá aumentar cerca de 30% em poucos anos, dessa forma a indústria tem buscado outras formas para fornecer o suprimento suficiente de produtos ao mercado, como o desenvolvimento de equivalentes ou substitutos de manteiga de cacau e a busca por novas fontes lipídicas semelhantes.

Para que uma nova fonte lipídica seja considerada boa substituta ela deve apresentar características físicas, texturais e de cristalização e/ou derretimento semelhantes aquelas da gordura ou óleo primário, pois assim, qualquer produto baseado na alternativa corresponderá ao original. Isso pode ser alcançado a partir de uma variedade de óleos e gorduras modificados, especialmente interesterificados (ROHM *et al.*, 2018), mas também de fontes naturais, sejam frações ou misturas, que não só correspondem ao perfil de fusão da fonte primária como também são uma boa combinação em composição de ácidos graxos. No caso da manteiga de cacau, por exemplo, são considerados bons substitutos gorduras derivadas dos óleos de palma, côco e outras palmeiras láuricas e as manteigas de karité ou da semente de manga (JAHURUL *et al.*, 2013; TALBOT, 2015; BEG *et al.*, 2017).

1.2 Emulsões

Os alimentos são misturas complexas de substâncias, sendo que algumas são consideradas incompatíveis. Assim a maioria dos alimentos, sejam naturais ou processados, consistem em emulsões, parciais ou totais, ou estiveram em estado de emulsão em algum momento durante sua produção, especialmente aqueles com alto teor lipídico ou ainda possuem algum ingrediente específico que é uma emulsão (WALSTRA & VAN VLIET, 2010).

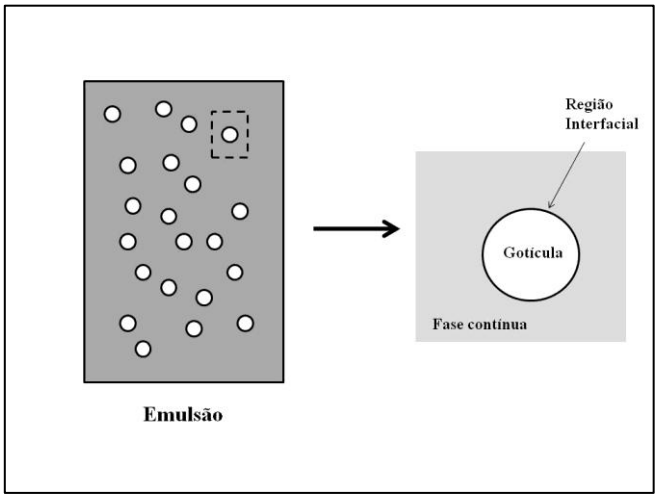
1.2.1 Composição das Emulsões

Uma emulsão consiste em dois líquidos imiscíveis, geralmente denominados de água e óleo, onde o termo "água" representa qualquer fase aquosa ou polar (como por exemplo, água pura, uma solução salina ou líquido iônico), enquanto óleo representa qualquer substância hidrofóbica ou insolúvel em água, como por exemplo os lipídios (SILVA *et al.*, 2016), sendo um deles disperso como pequenas gotículas (fase dispersa) no outro (fase contínua), e separados por uma interface composta por substâncias surfactantes (Figura 6) (McCLEMENTES, 2015).

Geralmente as emulsões são classificadas de acordo com a distribuição espacial relativa das suas fases, onde um sistema que consiste em gotículas de óleo dispersas na água é chamado de emulsão óleo em água (O/A), por exemplo, molhos para saladas e maionese; e um sistema que consiste em gotículas de água dispersas em uma fase oleosa é chamado de emulsão de água em óleo (A/O), como a margarina ou outros cremes vegetais, e ainda, dispersões ou emulsões sólidas, que são pequenas partículas sólidas dispersas em uma fase aquosa ou lipídica, como o chocolate (McCLEMENTES, 2015). Além dessas, emulsões múltiplas também podem ser formadas, como as do tipo óleo em água em óleo (O/A/O) ou de água em óleo em água (A/O/A), que consistem em gotículas de uma fase dispersa (denominadas gotículas internas) que estão espalhadas dentro de gotículas de outra fase (gotículas externas) que por fim é circundada pela fase contínua, esse tipo de emulsão ainda é pouco utilizado na indústria, sendo as principais aplicações os sistemas de incorporação, preservação ou liberação de nutrientes e compostos bioativos ou terapêuticos, seja na indústria de alimentos ou farmacêutica (JIMÉNEZ-COLMENERO, 2013; SILVA *et al.*, 2016; McCLEMENTES, 2017).

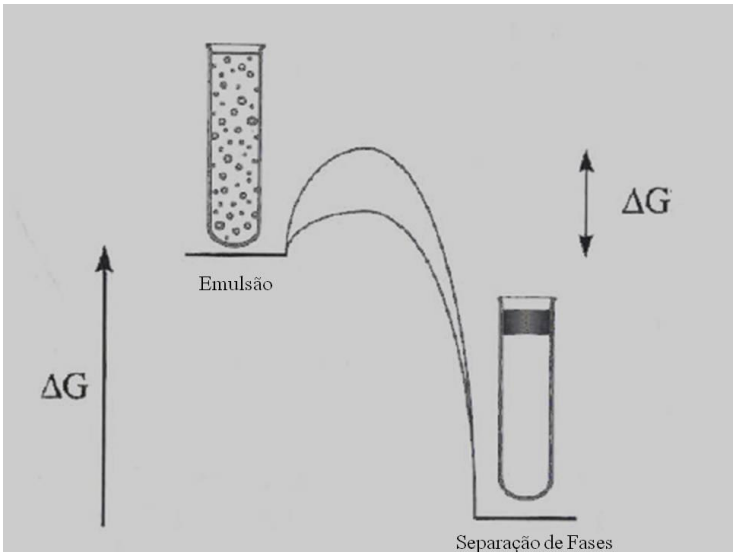
Como água e óleo são substâncias incompatíveis, possuem características químicas e físicas muito diferentes e baixa interação molecular, as emulsões são consideradas sistemas termodinâmicamente instáveis, dessa forma, a separação entre as duas fases em duas camadas puras distintas é rápida, pois assim elas possuem menor quantidade de energia livre (Figura 7) (BERTON-CARABIN *et al.*, 2018). Então, para aumentar a estabilidade cinética do sistema são adicionadas substâncias estabilizadoras, sendo as principais os emulsificantes (OZTURK & McCLEMENTS, 2016; PENGON *et al.*, 2018) e os agentes de textura (FARJAMI & MADADLOU, 2019; FENG *et al.*, 2019; SHAKEEL *et al.*, 2019).

Figura 6. Ilustração de uma emulsão e uma gotícula mostrando as diferentes fases e a região interfacial.



Fonte: Adaptado de McClements (2015).

Figura 7. Energia livre (ΔG) e separação de fases das emulsões.



Fonte: Adaptado de McClements (2015).

Emulsificantes são moléculas de superfície ativa, ou seja, possuem uma parte hidrofílica e outra hidrofóbica, o que as torna capazes de adsorver na interface óleo-água e impedir ou retardar a coalescência das gotas, seja por forças eletrostáticas de repulsão entre as gotículas e/ou a interações estéricas, devido a sobreposição das moléculas interfaciais que se aproximam (BERTON-CARABIN *et al.,* 2018; BERTON-CARABIN & SCHROËN, 2019). Existem três categorias principais de emulsificantes alimentares: i) aqueles com baixo peso molecular, que são representados pelas lecitinas, polissorbatos e mono ou diglicerídeos; ii) os biopolímeros anfifílicos, como as proteínas e polissacarídeos, especialmente as proteínas do leite e da soja e gomas; e iii) partículas sólidas coloidais, sejam de origem inorgânica ou natural a partir de amidos, proteínas e lipídios, sendo que quando este tipo de estabilizante é utilizado as emulsões são comumente chamadas de emulsões de *Pickering* (KRALOVA & SJÖBLOM, 2009; McCLEMENTS & GUMUS, 2016; TAVERNIER *et al.,* 2016; SCHRÖDER *et al.,* 2017).

Os modificadores de textura podem ser divididos em duas categorias, dependendo do modo de ação na mistura, em espessantes ou geleificantes. Agentes espessantes são ingredientes utilizados para aumentar a viscosidade da fase contínua das emulsões, enquanto os agentes geleificantes são ingredientes usados para formar um gel na fase contínua, ambos melhoram a estabilidade das emulsões pela barreira e dificuldade que impõe aos movimentos das gotículas da fase dispersa evitando que ocorra coalescência, floculação ou sedimentação. Na indústria de alimentos, os agentes espessantes e geleificantes mais usados são geralmente polissacarídeos ou proteínas em emulsões O/A e cristais de gordura ou ceras em emulsões A/O (McCLEMENTS, 2012; MARKU *et al.,* 2012; McCLEMENTES, 2015; SAGIRI *et al.,* 2015; FARJAMI & MADADLOU, 2019; SHAKEEL *et al.,* 2019; FENG *et al.*, 2019).

A natureza dos ingredientes de uma emulsão está intimamente ligada à estabilidade do sistema. As interações moleculares possíveis em cada tipo de gordura dependem muito de sua organização em triacilgliceróis. De modo geral, as principais interações dos lipídios são a atração de van der Waals e a repulsão estérica, a força dessas interações depende do tamanho das cadeias dos ácidos graxos, grau de saturação ou insaturação e também simetria da molécula do triacilglicerol. Ácidos graxos de cadeia mais longa, saturados e organizados de modo simétrico são mais apolares e por isso a emulsão tende a ser menos estável do que quando o óleo presente na emulsão é constituído por cadeias acila mais curtas ou insaturadas (McCLEMENTES, 2015).

Além disso, em emulsão do tipo A/O, a criação de produtos alimentares estáveis e com propriedades desejáveis depende da compreensão dos principais fatores que podem influenciar a cristalização e o derretimento de lipídios nos sistemas emulsionados. A força das ligações entre as moléculas de gordura é maior no estado sólido do que no estado líquido, isso porque elas são capazes de empacotar e formar redes de cristais de gordura (McCLEMENTES, 2015). A dureza dessa rede é determinada também pela natureza dos ácidos graxos e organização deles na molécula de triacilglicerol, ácidos graxos com cadeias maiores, mais saturadas e organizados simetricamente tem empacotamento mais próximo e por isso formam uma rede gordurosa mais forte, dura, e consequentemente, com ponto de fusão mais altos (BAYÉS-GRACIA *et al.*, 2015; LIU *et al.*, 2018a), assim muitas vezes a estabilidade da emulsão depende da formação dessa rede gordurosa e das condições de armazenamento para manter a rede.

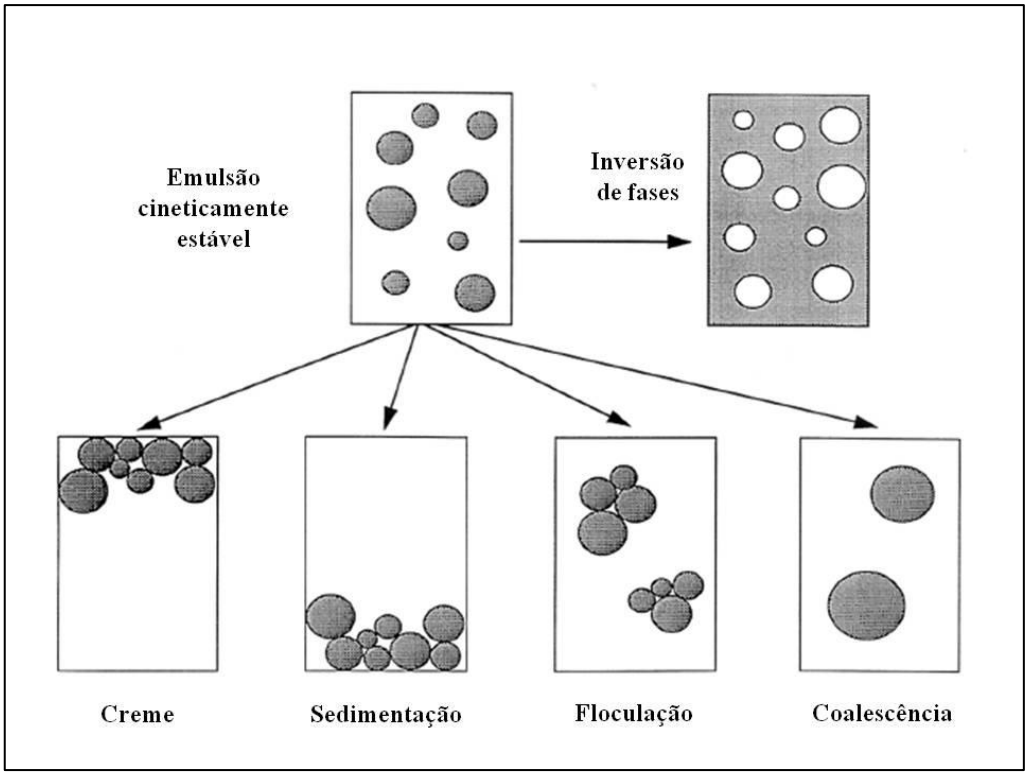
1.2.2 Estabilidade das Emulsões

Para que uma emulsão seja formada é necessário promover a homogeneização dos seus componentes, isso é alcançado pela diminuição no tamanho das partículas da fase dispersa e é conseguido através da mistura e cisalhamento das fases (GHOSH *et al.*, 2013; McCLEMENTS, 2015). Após a formação da emulsão os principais fatores que irão afetar a estabilidade do produto formado são as características de cada uma das fases, dispersa e contínua, o tamanho médio das gotas e as condições de armazenamento das emulsões (BERTON-CARABIN *et al.*, 2018; RICAURTE *et al.*, 2018).

A desestabilização física das emulsões está intimamente ligada aos componentes da mistura e ocorre principalmente pela formação de creme ou sedimentação de uma das fases e também pela coalescência de gotas (Figura 8). (McCLEMENTS, 2005; LEAL-CALDERON *et al.*, 2007). O creme e a sedimentação são resultantes da diferença entre as densidades nas fases, que neste caso é a força motriz para que as moléculas semelhantes se agrupem. Esse tipo de separação pode ser retardado pela diminuição do tamanho das gotas ou aumento na viscosidade

da fase contínua o que promove valores mais equilibrados para a diferença de densidades das fases.

Figura 8. Mecanismos físicos de desestabilização de emulsões.



Fonte: Adaptado de McClements (2015).

A floculação envolve a agregação de duas ou mais gotículas da emulsão para formar flocos que podem precipitar ou flotar. Neste caso, o que leva a instabilidade são as forças atrativas das interações moleculares entre as gotículas que superam as forças repulsivas, sejam eletrostáticas e/ou estéricas, esse defeito pode ser causado por falta ou excesso na concentração dos emulsificantes (GUZEY & McCLEMENTS, 2006; DICKINSON, 2009).

Para que ocorra coalescência de gotículas, o filme interfacial em torno das gotas em contato precisa se romper, levando à fusão de gotículas e progressivamente à formação de gotas muito grandes ou regiões distintas na emulsão, que constituem um defeito de aparência na maioria das emulsões e geralmente está relacionado ao tipo e/ou baixa concentração dos agentes de superfície (GUZEY & McCLEMENTS, 2006; LEAL-CALDERON *et al.*, 2007; DICKINSON, 2009; McCLEMENTS, 2015).

O tamanho das gotículas em uma emulsão tem um forte impacto em sua estabilidade. Quanto maior o tamanho das gotas menor a área interfacial total, o que leva ao aumento da energia livre (ΔG) e torna termodinamicamente mais favorável a separação das fases e

instabilidade da mistura, conforme equações 2 e 3 (LEAL-CALDERON *et al.,* 2007; McCLEMENTS, 2015; BERTON-CARABIN *et al.,* 2018).

$$\Delta G = \gamma \Delta A \tag{2}$$

$$A_{Sup} = \frac{3}{r\rho} \tag{3}$$

Onde: ΔG é a variação da energia livre de Gibbs (J), γ é a tensão interfacial entre as gotas e a fase contínua (N/m), ΔA é a mudança na área superficial do sistema, A_{Sup} é a área superficial específica do sistema (m²/g de fase dispersa), r é o raio da gota (m) e ρ a densidade da fase dispersa (g/mL).

Além da estabilidade, outras características como luminosidade, cor, viscosidade e cremosidade da emulsão também são influenciadas pelo tamanho das gotas (McCLEMENTS, 2007). A maioria dos alimentos apresentam emulsões com gotículas de diâmetros na faixa entre 0,1 e 100 μm e são caracterizadas como microemulsões (McCLEMENTS, 2007; McCLEMENTS, 2015). Entretanto, atualmente a indústria de alimentos tem demonstrado um interesse crescente na utilização de emulsões com diâmetros menores (d <0,1 μm), que são as nanoemulsões, principalmente como meio para transporte, proteção e liberação de certos ingredientes, especialmente corantes, aromas, sabores e nutracêuticos (CAROCHO *et al.,* 2014; CHATZIDAKI *et al.,* 2015; FU *et al.,* 2016; CARVALHO *et al.,* 2018; RAVIADARAM *et al.,* 2018) e para redução dos teores totais de gordura em produtos alimentícios à base de emulsão (SULLO *et al.,* 2014; SAGIRI *et al.,* 2014; PROSAPIO & NORTON, 2019).

As condições de armazenamento, em destaque as mudanças no pH da emulsão e variações de temperatura, são muito importantes para avaliação e manutenção da estabilidade das emulsões. Tais variações podem influenciar a capacidade de estabilização dos emulsificantes, por exemplo, proteínas ou outras moléculas com grupos carregados, que podem ter sua estrutura modificada a depender do pH do meio. E condições de aumento ou diminuição da temperatura influenciam as propriedades térmicas como densidade, viscosidade e tensão interfacial das fases dispersa e contínua, podendo levar a coalescência das gotículas, floculação e formação de creme (RAGHAVENDRA & RAGHAVARAO, 2010; RICAURTE *et al.,* 2018).

Além disso, alguns produtos alimentícios, como os sorvetes, as margarinas ou cremes vegetais e chocolates, são armazenados em temperaturas baixas ou possuem gorduras com ponto de fusão mais alto. Dessa maneira, a cristalização das gorduras também é um ponto de cuidado na estabilidade das emulsões nestes produtos. Para esses tipos de produtos, as propriedades

físico-químicas de maior interesse são: as temperaturas de transição de fase dos lipídios (líquido-sólido), a variação do teor de gordura sólida com a temperatura, a morfologia, interações e localização dos cristais dentro das gotículas e o empacotamento das moléculas de gordura dentro dos cristais, pois elas terão grande influência sobre a estabilidade geral e propriedades físicas da emulsão (McCLEMENTS, 2007; SULLO *et al.*, 2014; SAGIRI *et al.*, 2014; BAHARI & AKOH, 2018).

1.2.3 Aplicação de Emulsões A/O na Indústria de Alimentos

As emulsões A/O são amplamente aplicadas em diversos setores industriais, como o de cosméticos, por exemplo, em batons, cremes e loções (LE RÉVÉREND *et al.*, 2011; MARTINEZ *et al.*, 2019), de produtos farmacêuticos, através do encapsulamento e distribuição de drogas (MELNIKOV *et al*., 2017) e em alimentos, como pães, bolos, biscoitos, massas, recheios e coberturas, sobremesas cremosas, sorvetes, refeições prontas congeladas, molhos, entre outros (ARELLANO *et al.*, 2015; TALBOT, 2015; GUILLÉN *et al.*, 2016; PINTO *et al.*, 2018; WAGHMARE *et al.*, 2018; BEIDOKHTI & JÄGER, 2017; HALIM *et al.*, 2018; ZEMBYLA *et al.*, 2020).

Os cremes vegetais ou *shortenings* são as emulsões de base lipídica mais importantes para a indústria. Eles são fabricados tanto para o consumidor final (por exemplo, as margarinas de mesa) como também, para uso como ingredientes de outros produtos, que são as gorduras ou cremes vegetais especiais (GUILLÉN *et al.*, 2016). Neles, a fase aquosa é dispersa como gotículas em óleo líquido que é estabilizado por uma rede de cristais de gordura sólidos, sendo a composição da fase lipídica cuidadosamente formulada para ter a proporção necessária entre óleo líquido e gordura sólida. A presença da quantidade adequada de cristais é fundamental, pois eles tem dupla funcionalidade, garantir a estabilidade e conferir textura ao produto.

A gordura cristalizada é adsorvida na interface água-óleo e forma uma concha ao redor das gotas de água, proporcionando assim uma barreira física interfacial contra a coalescência e promovendo a estabilidade (FRASCH-MELNIK *et al.*, 2010). O tipo de óleo e sua composição em triacilgliceróis, e consequentemente tipo de cristal (α, β ou β’), são os responsáveis pela textura, consistência plástica e espalhabilidade adequada, além de boas propriedades de fusão (ARELLANO *et al*., 2015).

Óleos como de soja, girassol, canola, palma, e oliva (líquidos) e palmiste e coco (sólidos) e/ou suas frações oleínas (líquidas) e estearinas (sólidas), são os mais utilizados na indústria para a produção das margarinas e cremes (MAKERI *et al.*, 2019). Eles podem ser misturados, interesterificados ou hidrogenados total ou parcialmente, sendo que a combinação da variedade

de matérias-primas e dos métodos de processamento tem influência decisiva em sua composição e posterior aplicação (ARELLANO *et al.,* 2015; MITSOU *et al.,* 2016; GUILLÉN *et al.,* 2016; SARAFHANA *et al.,* 2016; ROHN *et al.,* 2018). Além destes, outros óleos e gorduras, de fontes vegetais não convencionais, tem sido sugeridos para fabricação dos cremes vegetais, principalmente como forma de diminuir as quantidades de gorduras *trans* resultantes de processos como a hidrogenação parcial dos óleos mais utilizados industrialmente (YAMONEKA *et al.*, 2019; MAKERI *et al.*, 2019).

Atualmente, os cremes vegetais ou emulsões A/O, além de contribuírem para as características estruturais, sensoriais e nutritivas desejáveis de muitos produtos processados (WASSELL *et al.,* 2010; PATEL *et al.,* 2020) são utilizadas também como estratégia para reduzir o teor de gordura (DI BARI *et al.*, 2014, 2017; LUO *et al.,* 2019), para encapsular compostos bioativos hidrofílicos e para controlar a liberação de diferentes compostos encapsulados (NADIN *et al.*, 2014; ZHU *et al.*, 2019; CELLI & COMUNIAN, 2021), como antioxidantes (MOSCA *et al.,* 2013; KATSOULI *et al*., 2017), vitaminas (KHALID *et al.,* 2013), aminoácidos (BHATTI *et al.,* 2017), minerais (MÁRQUEZ *et al.*, 2010; LI *et al*., 2013; ZHU *et al.*, 2016) e probióticos (PICONE *et al.*, 2017) entre outros.

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Capítulo 2

Objetivos

1 OBJETIVOS

1.1 Objetivo Geral

Apresentar o potencial tecnológico do óleo bruto de babaçu (*Orbignya phalerata Mart.*), com vistas à utilização na indústria de alimentos, através da caracterização química, física e térmica de óleos obtidos por diferentes métodos de extração e sua aplicação na formulação de um sistema lipídico utilizado como ingrediente para a indústria.

1.2 Objetivos Específicos

a. Determinar a composição química (perfil em ácidos graxos e triacilgliceróis) e parâmetros de qualidade (pH, cor, matéria volátil, índices de refração, de acidez, de peróxidos, de saponificação e de iodo) dos óleos brutos de babaçu obtidos por diferentes formas de extração, por cozimento das amêndoas (VBO) e por prensagem mecânica das amêndoas do coco babaçu (EVBO);
b. Determinar as propriedades térmicas, densidade, viscosidade, calor específico e tensão interfacial, dos diferentes óleos brutos de babaçu (VBO e EVBO);
c. Determinar o comportamento térmico dos óleos brutos de babaçu (VBO e EVBO) por meio da calorimetria e determinação da fusão, da cristalização e da decomposição térmica dos óleos;
d. Determinar, através de ensaios *in vitro*, a capacidade antioxidante dos óleos brutos de babaçu (VBO e EVBO) e quantificar alguns de seus compostos bioativos (flavonoides, ácidos fenólicos, tocoferóis e carotenoides);
e. Formular diferentes emulsões (A/O) tendo como fase contínua o óleo bruto de babaçu (BO) em mistura com a manteiga de cacau (CB) em diferentes proporções, para aplicação na indústria de alimentos;
f. Caracterizar as diferentes emulsões quanto as suas propriedades físico-químicas (pH, condutividade elétrica, tamanho de gota, derretimento e polimorfismo dos lipídios), propriedades mecânicas (dureza e espalhabilidade) e estabilidade (*cracking*, índice de *creaming* e ensaio de estabilidade térmica acelerada) em diferentes condições de armazenamento e identificar as aplicações tecnológicas mais adequadas para os cremes vegetais obtidos.

Capítulo 3

Artigo 1

Physicochemical and thermal characterization of babassu oils (*Orbignya phalerata Mart.*) obtained by different extraction methods

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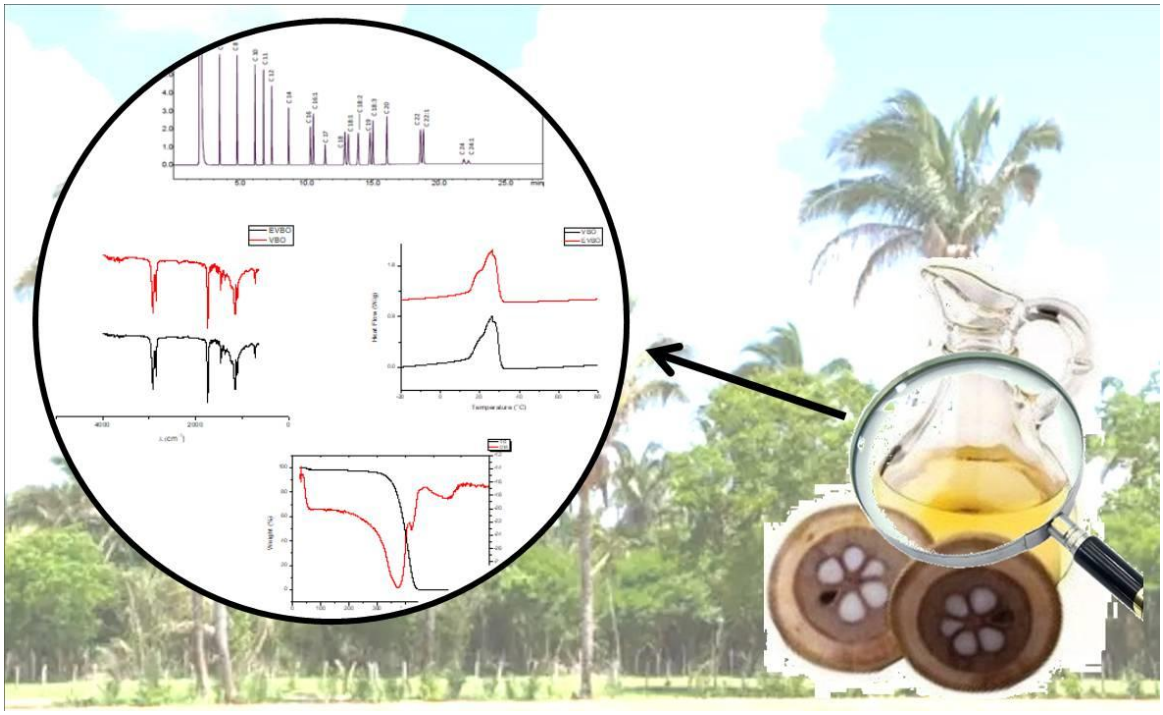
GRAPHICAL ABSTRACT



Physicochemical and thermal characterization of babassu oils (*Orbignya phalerata Mart.*) obtained by different extraction methods.

PHYSICOCHEMICAL AND THERMAL CHARACTERIZATION OF BABASSU OILS (*Orbignya Phalerata Mart.*) OBTAINED BY DIFFERENT EXTRACTION METHODS

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Abstract

Babassu oil is a raw material widely used in the pharmaceutical and biofuels industry. However, its physical-chemical and thermal characteristics are not widely described in the literature. This article describes these characteristics and, thus, seeks to increase the application of this raw material in the food industry. In this work, two different types of babassu oils, extra-virgin and virgin, were studied. The physicochemical characteristics, lipid profile, composition of the triacylglycerol and thermal properties of both oils were determined. Moreover, the crystallization and melting behavior was determined and the FTIR-ATR spectra of the oils acquired. The results show that the main fatty acids present are medium-chain and the type of extraction modifies the amounts of fatty acids present in each type of oil. Despite this, its physical-chemical characteristics and thermal properties are the same, except color and thermal stability, where extra-virgin oil is lighter and more stable than virgin babassu oil.

Keywords: *Orbignya phalerata Mart.*; vegetable oil; raw material for food industry; fatty acids; TAG; DSC; TGA; thermal properties.

Abbreviations:DSC – Differential Scanning Calorimeter; FA – Fatty Acids; FTIR-ATR – Fourier Transform Infrared by of the Attenuated Total Reflection; EVBO – Extra Virgin Babassu Oil; TAG – Triacylglycerols; TGA - Thermogravimetric Analysis; VBO – Virgin Babassu Oil.

1. Introduction

Vegetable oils and fats are those extracted from parts of plants, such as seeds, kernels, flowers, leaves and fruit and vegetable pulp. They are mostly composed of triacylglycerols (Indelicato et al., 2017), which are structures formed by three molecules of fatty acids esterified with a glycerol molecule. They also contain free fatty acids, monoacylglycerols and diacylglycerols and other minor compounds such as sterols, phospholipids, fat-soluble vitamins, pigments and minerals (Dijkstra, 2016; Savva & Kafatos, 2016).

The fatty acid composition of vegetable oils is determined by different factors, in particular the botanical source, genetic variations (Kumar, Sharma & Upadhyaya, 2016); climate, soil and planting management (Santos et al., 2013); in addition to the type of processing and degree of refining (Dia, Garcia, Mabesa & Tecson-Mendoza, 2005; Aquino et al., 2012; Sampaio et al., 2019). Oils from oilseeds are rich in polyunsaturated fatty acids (Savva & Kafatos, 2016). Fruit pulp oils, such as oil palm and olive, have a high amount of antioxidant compounds (Ghazani & Marangoni, 2016) and palm kernel oils have a large amount of saturated fatty acids (Bauer, Damásio, Da Silva, Santana, Gualberto & Simionatto, 2013; Oliveira, Neves, Ribeiro, Lopes & Silvério, 2016). Because of this, research into new sources of vegetable oils is important for the development of new products. One of these source is palm oil from the *Orbygnia* genre.

The *Orbygnia* genus is composed of over 36 different palm species that are found in Central and Southern America, especially Mexico, Peru, Bolivia, and Brazil (Hiura & Rocha, 2018). *Orbignya phalerata Mart*. (babassu) is one of the most important palm species in Brazil. This palm can reach between 10 and 30 meters in height and presents up to five bunches that produce from 250 to 500 fruits (coconuts), each of them having between 3 and 5 kernels (Santos et al., 2017). Babassu fruit is widely consumed in the North and Northeast regions of Brazil and is considered an important resource, both in economic and nutritional terms. This is mainly related to the exploitation of the culture, which is essentially extractive and / or subsistence, its main product being the babassu oil (Oliveira, Neves, Ribeiro, Lopes & Silvério, 2016). The oil is used locally in food, soap and cosmetics and exported when there is a shortage of palm kernel or coconut oil.

Oil extraction it is mainly handcrafted and the annual output is about 57000 tons (IBGE, 2015), but can be increased due to the high productivity of babassu palm trees. As for the processing, vegetable oils are commonly extracted through cold or temperature controlled mechanical pressing or through the use of organic solvents. From the babassu almonds are extracted two types of oil: extra-virgin babassu oil (EVBO) and virgin babassu oil (VBO).

EVBO is obtained by cold pressing whole, healthy almonds without yellowing or superficial physical damage, followed by decantation, filtration and packaging. The VBO is obtained by crushing previously selected and toasted almonds, followed by baking the mass to obtain the oil, which is separated by decanting, filtered and reheated for total removal of the water resulting from the cooking step and then packaged.

The babassu oil is rich in saturated fatty acids (80-91%), with emphasis on lauric, myristic, palmitic, capric, caprylic and stearic acids. The remainder are unsaturated fatty acids (9-20%), where oleic acid and linoleic acid are present (Oliveira, Neves, Ribeiro, Lopes & Silvério, 2016). This composition is similar to that of palm kernel and coconut oils, which are the most commonly produced and consumed vegetable oils (USDA, 2019).

Palm oils are considered particularly special to industry due to their lipid profile presenting unique characteristics for industrial application. These oils are nutritious, resistant to oxidation and easily absorbed, semi-solid or solid at refrigeration temperature, and have fatty acids considered as moisturizers and emollients (Dijkstra, 2016). The so-called lauric fats, such as babassu oil, can be used in the manufacture of cosmetics and personal care products, ointments and pharmaceutical creams (Talbot, 2015), supplements for special diets and in cooking and frying applications, ice products, baking, creams and fillings (Arellano, Norton & Smith, 2015; Smith, 2015).

Currently, babassu oil is little used by the food industry, its production is almost completely destined for the cosmetic and pharmaceutical industry (Gumiero & Rocha Filho, 2012; Amaral et al., 2014; Reis et al., 2017) or biodiesel (Paiva, Da Silva, Barboza, De Oliveira, De Castro & Giordani, 2013; Da Rós, Costa e Silva, Grabauskas, Perez & Castro, 2014), which may be related to the greater number of investigations regarding its characteristics that are important for these segments. In relation to the food industry, the quantity of research related to babassu oil is limited (Machado, Chaves & Antoniassi, 2006; Ferreira, Faza & Le Hyaric, 2012). In general, data on its chemical, physical and thermal characteristics are scarce in the literature, which consequently reduces its application in this industry. Therefore, the objective of this study was the lipid, physical and thermal characterization of two types of babassu crude kernel oils, one extracted by cold mechanical pressing and the other extracted by cooking the mass of roasted and crushed kernels (heat extraction).

2. Material and Methods

2.1 Samples

Samples of crude babassu kernel oils were purchased directly from producers in the states of Tocantins and Maranhão, Brazil. Samples, extra virgin babassu oil (EVBO) and virgin babassu oil (VBO), were purchased fresh immediately after extraction from three different batches in December 2016.

2.2 Physicochemical Characteristics

All determinations for the physicochemical characteristics (moisture and quantity of volatile matter, ash content, acid number, peroxide index, saponification index, iodine number, refractive index, density at 25°C and color) of the babassu oil samples, EVBO and VBO, were performed in triplicate according to protocols described below.

The moisture and quantity of volatile matter were determined following the methodology 920.151 (AOAC, 2010). The determination of the ash content was carried according to Ca 11-55 method (AOCS, 2012).

Acidity (% of free fatty acids), peroxide (mEq active oxygen/g of babassu oil) and saponification (mg KOH/g of babassu oil) were obtained by titrating the samples of the different oils followed, respectively, methods Cd 3d-63, Cd 8-53, Cd 3c-91 (AOCS, 2012). The iodine levels of triglycerides and free fatty acids were calculated after determination of the fatty acid composition of babassu oils, following the method Cd 1c-85 (AOCS, 2012).

Determination of specific extinction by absorption in the ultraviolet region was performed by reading absorption at the wavelengths of 232 and 270 nm. These lengths identify the presence of conjugated diene and triene systems, respectively. Specific extinction at each wavelength, for both EVBO and VBO, was calculated as described in Method Ch 5-91 (AOCS, 2012).

To obtain the refractive indices (RI) of babassu oils, a Q767BD digital refractometer (Quimis, Diadema, Brazil) was used. . This equipment was connected to a thermostatic bath (Tecnal, Te-184, Piracicaba, Brazil) that allowed temperature control at 40°C. The refractive index was calculated according to the method Cc 7-25 (AOCS, 2012).

The color of the oils was determined in a Minolta colorimeter (Konica Minolta, Ramsey, New Jersey, USA) with CIELAB system, which considers the L^* coordinates for lightness (black/white), a^* and b^* for chromaticity, from green to red and blue to yellow, respectively.

The density (kg/m³) of the samples was determined using a DMA 5000M Digital Bench Density Meter (ANTON PAAR, Graz, Austria). The density of the samples being measured at 25°C and the density variation in function of the temperature was determined in the range of 30°C to 80°C.

The viscosity (Pa.s) of the samples was determined by a Searle rotary concentric cylinder viscometer (Rheotest 2.1, Ottendorf-Okrilla, Germany). The apparatus was coupled to a thermostated bath (Marconi MA-184, São Paulo, Brazil) capable of maintaining the temperature. The variation of the viscosity of the oils as a function of temperature was determined in the range of 30°C to 80°C.

The oil/air and oil/water interfacial tension (mN/m) was determined by the Du Noüy ring method using a Lauda TD1C tensiometer (Lauda GmbH, Königshofen, Germany) equipped with a 19.1 x 10^{-3} m platinum ring of diameter. The equipment was calibrated before the measurements and the readings were corrected according to the equation described by the manufacturer. The variation in interfacial tension as a function of temperature was determined in the range of 30°C to 80°C.

2.3 Lipid Profile

2.3.1 Identification and Quantification of Fatty Acids

For the identification and quantification of fatty acids (FA), the samples of crude babassu kernel oil were transesterified to obtain methyl esters of fatty acids, according to the procedure of Bannon, Craske, Hai, Harper & O'Rourke (1982). The fatty acid esters were separated in GC-2010 Plus Shimadzu (Kyoto, Japan) gas chromatograph equipped with Flame Ionization Detector, Restek Rt-2560 fused silica capillary column (120m, 0.25mm di, 0.20µm of thickness) and Aoc-20i self-injection system (Shimadzu). The operating parameters established were: injector and detector temperatures, 140°C and 260°C, respectively. The column temperature was programmed at 140°C for 5 min, followed by a heating ramp of 3°C/min up to 245°C, remaining at this temperature for 20 min. The total analysis time was 60 min. The gas flows (White Martins) were 40 mL/min for the hydrogen, 30 mL/min for the nitrogen and 400 mL/min for the synthetic air. Injections were performed in triplicate and the injection volumes were 1.0 µL. The peak areas of the fatty acid methyl esters were determined using GC Solution software (Shimadzu, Kyoto, Japan).

The identification of FA was performed by comparing sample retention times with a standard containing a mixture of fatty acid methyl esters (FAME Mix C4-C24, Supelco, USA) analyzed under the same operation conditions. Results were expressed as percentages relative to total fatty acids.

2.3.2 Profile for Acylglycerols

The acylglycerol profile (g/100 g oil) of the samples (EVBO and VBO) was identified using the method Cd 11b 91 (AOCS, 2012). The monoacylglycerols and diacylglycerols were converted to their respective trimethylsilylesters via derivatization with Bis (trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS).

The trimethylsilyl ethers were analyzed by an Agilent gas chromatograph (Saint Claire, USA) equipped with Flame Ionization Detector, fused silica capillary column (25m, 0.25mm d.i) and self-injection system. The operating parameters established were: injector and detector temperatures, 320°C and 350°C, respectively. The column temperature was programmed at 80°C for 5 min, followed by a ramp of 10°C/min until 360°C, remaining at this temperature for 15 min. The total analysis time was 48 min. The flow of the entrainment gas (Helium) was 5 mL/min. Injections were performed in triplicate and the injection volumes were 1.0 μL. The peak areas of the trimethylsilyl ethers were integrated through the equipment software.

Identification of monoacylglycerols and diacylglycerols was performed by comparing sample retention times with a standard containing a mixture of glycerol, long chain fatty acids, monoacylglycerols, diacylglycerols and triacylglycerols (TAG) (Sigma, USA). The quantification of mono- and diacylglycerols was calculated according to Equation 1 and triacylglycerols were determined by difference between the total mass and the amount of the other analytes.

$$m_x = \frac{M_{IS} \times A_x}{R \times M_S \times A_{IS}} \quad (1)$$

In which:

m_x is the concentration of the analyte (mono or diacylglycerol) in g/100 g oil;

A_x is the area of trimethylsilylesters;

M_{IS} is the mass (g) of the internal standard added to the sample;

R is the response factor of the analyte;

M_S is the mass of sample (g);

A_{IS} is the area of internal standard.

TAG compositions were calculated from FA data via combinatorial analysis using the method described by Antoniosi Filho, Mendes & Lanças (1995). In this method, a model of random distribution (no preference to position sn-1,3 and sn-2) of FA in glycerol was used, hence only bulk FA composition was necessary as input data.

2.4 FTIR-ATR Analysis

The spectra of the EVBO and VBO samples were obtained through the FTIR-ATR Fourier Transform Infrared by of the Attenuated Total Reflection in the Agilent Cary® 630 equipment, under the medium infrared range, using the wavelength range from 4000 to 600 cm^{-1}, with resolution of 4 cm^{-1}, 64 scans and reading through the ATR diamond crystal.

2.5 DSC Analysis

The differential scanning calorimeter (DSC) analyses of babassu oils (EVBO and VBO) were performed on DSC-60A equipment (Shimadzu, Kyoto, Japan). About 10 mg of each sample were placed in an aluminum pan, which was then sealed using a sample pancreamer. The samples were heated to 100°C on the DSC instrument and held at this temperature for 10 min so that the previous history of the sample was erased. Samples were cooled to -30°C at a rate of -5°C/min. At the end of the period the sample was reheated to 100°C at a rate of 5°C / min and then cooled again in steps of 5°C/min to -30°C. The thermograms were recorded and the specific heat and the points of melting and crystallization of the two types of babassu oils.

2.6 TGA Analysis

The thermogravimetric analysis (TGA) of babassu oils (EVBO and VBO) were performed on DTA TG 60H equipment (Shimadzu, Kyoto, Japan). Approximately 10 mg of each sample was placed in an aluminum crucible. The samples were heated from 20°C to 750°C at a heating rate of 10°C/min and a dynamic nitrogen atmosphere at a flow rate of 50 mL/min. The thermograms were recorded and the thermal behavior of the different babassu oils revealed.

2.7 Mineral Content

The determination of the calcium (Ca), iron (Fe), magnesium (Mg) and phosphorus (P) contents of the EVBO and VBO oils was performed according to method D5185 – 13 (ASTM, 2013) with modifications. Approximately 1.0 g of each sample was homogenized in falcon tube. 9.0 g of V-Solv™ ICP Solvent organic solvent (LGC Standards, Manchester, USA) was added and the mixture was vigorously stirred until complete dissolution of the oil in the solvent. An analytical blank was prepared following the same procedure, omitting the sample and employing white mineral oil (Specsol, Quimlab, Jacareí, Brazil).

The quantification of the inorganic elements was performed in an inductive coupling plasma emission spectrometer (ICP OES 5100 VDV, Agilent Technologies, Tokyo, Japan) in axial view, equipped with a 27 MHz radio frequency (RF) source using an optical detector a peristaltic pump, a double step cyclonic nebulizer chamber, a 1.2 mm quartz torch and a seaspray nebulizer. The system uses, as liquid gas, high purity liquid argon (Air Liquide, São Paulo, Brazil).

The optimized operating conditions of ICP OES were: plasma power, 1.50 kW; argon flow rate, 15.0 L/min; auxiliary argon flow rate, 0.4 L/min; mist flow rate, 0.45 L/min; flow rate of the argon/oxygen mixture at 10%, number of replicates, 3; stabilization and readout time, 15s and wavelengths, Ca (317.933 nm); Fe (259.940 nm); Mg (280.270 nm); (213.618 nm).

The analytical curves for inorganic elements were prepared from 100 and 300 mg/kg multi-element organometallic standard dilutions (Conostan, SCP Science, Quebec, Canada) in the range of 0.011 to 10.900 mg/kg for Ca, Fe and Mg; and from 0.011 to 54.500 mg/kg for P. For all inorganic elements the analytical curves showed $R^2 > 0.9999$.

2.8 Statistical Analysis

The data obtained in this study, for chemical composition, physical and thermal properties were submitted to analysis of variance (ANOVA) using the SAS program, Studio version.

The fatty acids, mono, di and triacylglycerols, density at 25°C, specific heat, refractive index, volatile matter, saponification index, acid index, peroxide index, iodine content for free fatty acids and triglycerides, parameters of color L^*, a^* and b^* and inorganic elements were expressed as mean ± standard deviation and were compared using the F test ($p < 0.05$).

3 Results and Discussion

3.1 Physicochemical Characteristics

The physicochemical properties measured for babassu oils are presented in Table 1. For all measured properties the samples of babassu oils, EVBO and VBO, present values within the limits required by the regulations of the Codex Alimentarius Commission (2015) for the quality category of vegetable oil specified and edible. In general, these properties are related to the quality of the raw material, the processing and storage conditions and the fatty acid composition of these oils and fats. Values in accordance with those in the legislation indicate the potential of

babassu oil as an alternative raw material for the food industry. Regarding ash measurements, no significant amount of mineral waste was detected by the analysis method in any of the samples.

Table 1. Physicochemical characteristics of different types of babassu oil.

Physicochemical characteristic	EVBO	VBO
Density at 25°C (kg / m³)	918.630±0.011[a]	919.103±0.172[a]
Specific heat (kJ/kg.K)	2.789±0.129 [a]	2.155±0.313 [a]
Refractive index at 40°C	1.449±0.000[a]	1.449±0.000[a]
Volatile Matter at 105°C (% m / m)	0.023±0.004[a]	0.018±0.002[b]
pH	7.300±0.378[a]	7.300±0.346[a]
Saponification Index (mg KOH / g of oil)	249.665±2.477[a]	248.738±5.227[a]
Acidity Index (% lauric acid m/m)	0.086±0.004[a]	0.055±0.005[a]
Peroxide Index (mEq of active oxygen/kg of oil)	0.217±0.000[a]	0.916±0.291[b]
Free Fatty Acid Iodine Index (% m/m)	12.754±0.026[a]	14.254±0.027[a]
Triacylglycerol Iodine Index (% m/m)	12.204±0.138[a]	13.639±0.145[a]
Conjugated Dienes	2.531±0.184 [a]	2.850±0.000[b]
Conjugated Trienes	0.040±0.002[a]	0.302±0.033[b]
*L**	29.157±0.347[a]	24.379±0.425[a]
*a**	-0.743±0.032[a]	0.384±0.213 [b]
*b**	2.814±0.197[a]	-0.368±0.180[b]

Results presented as means ± standard deviations of the analyses of each type of babassu oil. Results followed by different letters in the same line are significantly different by the F-test at 5% probability.

The density, specific heat and refractive index measurements did not differ among the oils. They are used in the optimization of raw material quality control and processing parameters and vary mainly with the size of the carbon chains and degree of unsaturation of the fatty acids (Rojas, Coimbra & Telis-Romero, 2013). These measurements are useful in the control of hydrogenation processes (Machado, Chaves & Antoniassi, 2006) in order to evaluate the characteristics of each oil type, and frying (Kalogianni, Karapantsios & Miller, 2011), as well as indication and fraud detection (Torrecilla, García, García & Rodríguez, 2011).

The oils and the fats have different refractions and, according to their composition, they deviate the light rays that cross them. The RI of oil or fat increases with the length of the hydrocarbon chain and with the degree of unsaturation of the fatty acids constituting

triglycerides. It is also affected by the free fatty acids content, the oxidation level and the heat treatment of the product. The similar IR values for the two babassu oils analyzed, EVBO and VBO, indicate that, despite the more severe hot-picking steps, there were no significant changes in the refringance characteristics of the two oils. In addition, the increase in the VBO unsaturated fatty acid content may have offset the oxidation-related effects demonstrated by the different peroxide index values of the two babassu oils.

The moisture content is an important factor that determines the quality of the oil. The high moisture content increases the propensity of oil hydrolysis, leading to a higher free fatty acids content and rancid taste. Values below 0.2% m/m indicate a product of excellent quality (Alimentarius, 2015). Therefore, it can be stated that, with respect to moisture, both oils, EVBO and VBO, can be considered high quality products. The type of extraction influenced the amount of water in the final product being lower for the hot extracted oil (VBO) due to evaporation.

The chemical analysis showed that for the quality parameters acidity index, saponification index and iodine index there was no significant difference between babassu oils. The acidity index generally reflects the amount of hydrolyzed fatty acids in triglycerides. In crude oils it is used to predict the refining stages, in refined or virgin oils it is an attribute of quality used to measure hydrolytic rancidity. Low values, such as those presented by EVBO and VBO, indicate products of good quality and suitable for consumption.

The saponification value is related to the molecular weight of the fatty acids present in the oil, and the lower the saponification value, the longer the average length of the fatty acid chain. Higher values, such as those presented by babassu amond oil (≈ 249 mg KOH / g of oil), are compatible with its high content of medium chain fatty acids.

Iodine content is related to the degree of fatty acid unsaturation of the oils, lower values for iodine, such as those presented by EVBO and VBO, indicate a higher presence of saturated fatty acids (Pantoja, da Conceição, da Costa, Zamian & da Rocha Filho, 2013).

The peroxide index values were statistically different ($p < 0.05$) between the oils studied, with values for EVBO approximately 4.22 times lower than those presented by VBO. The process of cooking the mass of babassu kernels exposes the oil to high temperatures for prolonged periods of time. This process contributes to the oxidation of the oil and detection of the oxidation products, including hydroperoxides and aldehydes. Despite this, both EVBO and VBO presented values well below the limit considered unfit for consumption, which is up to 15 mEq O_2/kg of oil (Alimentarius, 2015).

During the heating processes, for example extraction, refining, cooking and frying, compounds with conjugated double bonds (dienes and trienes) may be formed. These compounds are formed from the oxidation of unsaturated fatty acids bound to glycerol or even

free unsaturated fatty acids. Therefore, the monitoring of these conjugated compounds can be a useful technique to study the quality of oils and fats and the processes to which they are submitted (Ribeiro, Polachini, Carvalho, Romero & Cabral, 2017). The babassu oils studied in this work have a low amount of unsaturated fatty acids, between 10 – 12%, consequently they also present low values for conjugated dienes and trienes. The differences detected among babassu oils reflect the severity of the treatments during the extraction stage, and the EVBO is considered of better quality than the VBO, since it presents inferior results.

Regarding color, the values for luminosity were similar, and significant differences ($p < 0.05$) were found for the chromaticity coordinates a^* and b^* of the two types of oils evaluated. Positive values for brightness indicate greater clarity of the sample, compatible with the translucent appearance of EVBO and VBO. The most negative values for a^* and more positive for b^* of EVBO are in accordance with their slightly yellowish coloration. In contrast, the most positive values for a^* and negative for b^* of the VBO reflect their darker coloration. This more intense coloring may be a result of the presence of pigments in the film covering the babassu kernel. These pigments are released during the cooking step and remain in the oil. In addition, the presence of proteins and carbohydrates in the babassu cake (Castro, Castilho & Freire, 2016), together with the heating during the oil extraction process, promote the oxidation and darkening reactions of VBO. One such reaction is the Maillard reaction, which occurs between the carbonyl groups of reducing sugars and the amino groups of amino acids, peptides or proteins It is catalyzed by heating and leads to the formation of melanoidins. Melanoidins are heterogeneous brown pigments and are responsible for the characteristic brown color of foods.

The results obtained for the thermodynamic properties of EVBO and VBO are presented in Table S1 in the Supplementary Material. These properties change as the temperature increases or decreases, as during, for example, the processing or storage of products, and may interfere not only with energy transfer, but with the fluidity and deformation, besides the structure of the food (Masood & Trujillo, 2016).

The density of both babassu oils, EVBO and VBO, vary between ≈ 915 to ≈ 880 kg/m³, for a temperature range of 30 ° C to 80 ° C. In oils and fats, the density is a result of the types of fatty acids in their composition, tending to decrease with the increasing numbers of unsaturation, the degree of saponification and the free fatty acids present, and when evaluated as a function of temperature, density behavior is inversely proportional to it (Ribeiro, Polachini, Carvalho, Romero & Cabral, 2017). Ribeiro and collaborators (2017), evaluated extra-virgin and low-quality olive oils, managed to demonstrate this variation, extra-virgin oils with higher values for density (≈909.79 kg / m³ at 35 °C) that make olives of lower quality and refined (≈909.15 kg / m³ at 35 °C). On the other hand, the viscosity tends to increase with the chain length of triglyceride

forming fatty acids and decreases with the degree of unsaturation, being a function of the size and orientation of the molecule. In relation to temperature, heating generally tends to decrease the viscosity of oils and fats (Ribeiro, Polachini, Carvalho, Romero & Cabral, 2017). Rojas, Coimbra & Telis-Romero (2013), studying different vegetable oils, showed that oils with higher levels of unsaturated acids and longer carbon chains, such as canola and sunflower, have lower densities (average of 919.9 kg / m³ at 20 °C) and higher viscosities (average of 78.96 mPa.s at 20°C). Oils with lower unsaturation levels and presence of shorter chain fatty acids, such as cotton and corn, have superior results for density (average of 929.1 kg / m³ at 20 °C) and lower viscosity (average of 61.07 mPa.s at 20°C). In this study, the viscosity of babassu oils, EVBO and VBO, showed values between 0.0038 - 0.008 Pa.s for the temperature range between 30 ° C and 80 ° C.

The interfacial properties of oils and fats are little affected by the triacylglycerol composition of these lipids, since the triacylglycerols exhibit very similar interfacial tension with each other and represent the largest portion in the composition of the oils. Thus, the variation of interfacial tension is related to the presence of different minor components such as free fatty acids, mono and diacylglycerols, phospholipids, phenolic compounds, compounds resulting from the oxidation of triacylglycerols, such as peroxides, aldehydes, ketones and alcohols (Dopierala et al., 2011). The surface tensions of the babassu oils, EVBO and VBO, presented essentially similar values and linear behavior decreasing (28.33 – 25.03 mN/m) as the temperature was increased (30 – 80 °C), values being concordant with the low oil/air interfacial activity.

The analysis of the interfacial tensions oil/water represents the interfacial activity between the surfaces of the two materials. The values were in the range of 11.70 – 12.15 mN/m, with values for EVBO slightly higher. These results reflect the composition of extra virgin babassu oil that has lower values for peroxides, monoacylglycerols and colored and phenolic compounds (Bauer et al., 2019), consequently less substances with high surface activity. The influence of the refining processes on the interfacial properties of palm oil has been demonstrated by Ho and Chow (2000), showing the influence of the minor components present in the oils.The higher the refining level or the number of refinement steps, the higher the interfacial tensions presented and consequently the lower the interfacial activities.

3.2 Lipid Profile

The results obtained for quantification of the fatty acids and acylglycerol profile of babassu oils are presented in Table 2.

Table 2. Quantification of fatty acids profile of the different types of oils.

Fatty Acid	Fatty Acid Content (%)	
	EVBO	VBO
Caproic acid (6:0)	0.5467±0.011[a]	0.545±0.019[a]
Caprylic acid (8:0)	7.509±0.093[a]	7.606±0.301[a]
Capric acid (10:0)	6.558±0.052[a]	6.808±0.252[a]
Hendecanoic acid (11:0)	2.097±0.032[a]	2.221±0.082[a]
Lauric acid (12:0)	47.747±0.343[a]	47.626±1.445[a]
Tridecylic acid (13:0)	1.478±0.032[a]	1.514±0.040[a]
Myristic acid (14:0)	14.224±0.084[a]	13.835±0.269[b]
Palmitic acid (16:0)	6.859±0.026[a]	7.300±0.092[b]
Palmitoleic acid (16:1)	0.215±0.003[a]	0.233±0.002[b]
Margaric acid (17:0)	0.008±0.011[a]	0.061±0.001[b]
Stearic acid (18:0)	2.897±0.008[a]	3.307±0.022[b]
Elaidic acid (18:1n9t)	0.091±0.001[a]	0.104±0.003[a]
Oleic acid (18:1n9c)	8.605±0.032[a]	9.567±0.099[b]
Linoleic acid (18:2n6)	0.273±0.0003[a]	0.311±0.002[b]
Linolenic acid (18:3n6)	1.365±0.005[a]	1.645±0.020[b]
Conjugated diene (18:2 9c 11t)	0.071±0.003[a]	0.0993±0.002[b]
Henecosanoic Acid (21:0)	Not detected	0.042±0.002[b]
Total Saturated	89.924	90.865
Total Unsaturated	10.076	9.135

Results presented as means ± standard deviations. Results followed by different letters in the same line are significantly different by the F-test at 5% probability.

Both the oil extracted by cold pressing (EVBO) and that extracted by the roasting and subsequent cooking of the mass of the babassu kernel (VBO) presented saturated fatty acids content approximately eight times higher than the unsaturated. The highest saturated fatty acid presents in EVBO and VBO associated with the low value of unsaturated fats indicate good resistance to oxidation (Redondo-Cuevas, Castellano, Torrens & Raikos, 2018) and are in agreement with other studies with babassu oil (Paiva, Da Silva, Barboza, De Oliveira, De Castro & Giordani, 2013; Oliveira, Neves, Ribeiro, Lopes & Silvério, 2016; Martini, Porto, de Oliveira & Sant'Ana, 2018) and oils from other palm trees, such as coconut (Dia, Garcia, Mabesa & Tecson-Mendoza, 2005) and licuri (Bauer, Damásio, Da Silva, Santana, Gualberto & Simionatto, 2013). Resistance to oxidation is a desirable characteristic of oils and fats as it ensures stability

during severe heat treatments applied in the food industry and consequently maintenance of the nutritional and sensorial quality of the products.

Table 3 presents the results for the composition in acylglycerols of the babassu kernel oils studied. The extraction process of babassu oil influenced the amounts of monoacylglycerols, the VBO presented higher amounts of monoacylglycerols than EVBO. This is the result of the combination of heat and water during the extraction stages, which favor the partial hydrolysis of triglycerides. As with most of the vegetable oils, babassu kernel oil, regardless of its extraction form, presented a high percentage of triacylglycerols (>99.0%), with 67.3% being trisaturated triacylglycerols. Binding of fatty acids to the glycerol backbone is related to the biosynthetic pathway of each plant and is therefore virtually specific.

Table 3. Acylglycerol composition of babassu kernels oil samples.

	Content of Acylglycerol (g/100g)	
Acylglycerol	EVBO	VBO
Monoacylglycerol	0.010±0.00[a]	0.160±0.014[b]
Diacylglycerol	0.425±0.001[a]	0.350±0.014[a]
Triacylglycerol (TAG)	99.565±0.015[a]	99.495±0.021[a]
	Content of TAG in percentage	
TAG code*	EVBO	VBO
LLL	14.465±0.037[a]	15.139±0.110[b]
LOL	12.547±0.035[a]	11.298±0.211[b]
LLM	10.335±0.041[a]	10.725±0.179[a]
LLC	8.451±0.005[a]	8.955±0.020[b]
LLCp	7.672±0.018[a]	8.115±0.029[b]
LLP	6.543±0.038[a]	7.041±0.172[a]
LOM	6.537±0.009[a]	5.801±0.049[b]
COL	4.946±0.016[a]	4.545±0.107[b]
CpOL	4.910±0.037[a]	4.481±0.128[b]

LLS	3.631±0.027[a]	4.068±0.130[b]
LOP	3.536±0.002[a]	3.319±0.003[b]
CpLC	2.799±0.014[a]	3.012±0.023[b]
LLnL	2.131±0.002[a]	2.095±0.040[a]
LOS	1.681±0.003[a]	1.662±0.000[a]
CpCpL	1.575±0.012[a]	1.688±0.000[b]
PPL	1.434±0.013[a]	1.650±0.000[b]
CpOC	1.187±0.010[a]	1.098±0.034[a]
LLnM	1.111±0.000[a]	1.075±0.010[b]
CpLnL	0.824±0.005[a]	0.821±0.024[a]
OLnL	0.794±0.002	Not detected
LLnP	0.603±0.001[a]	0.616±0.001[b]
CpOCp	0.534±0.007[a]	0.493±0.018[a]
SLP	0.528±0.006[a]	0.643±0.031[b]
MOS	0.416±0.001[a]	0.420±0.006[a]
CpCpC	0.408±0.005[a]	0.440±0.006[b]
LLiL	0.401±0.000	Not detected

*FA abbreviations: C, capric acid; Cp, caprylic acid; L, lauric acid; Li, linoleic acid; Ln, linolenic acid; M, myristic acid; O, oleic acid; P, palmitic acid; S, stearic acid.

Results presented as means ± standard deviations. Results followed by different letters in the same line are significantly different by the F-test at 5% probability.

The above results show that EVBO or VBO may be food sources of medium chain fatty acids (MCFA) and hence medium chain triglycerides (MCTs). The oils provide 64.48% of MCFA for EVBO and 63.35% of MCFA for VBO. MCFA are those containing 6 to 12 carbon atoms in their acyl chain, being the main constituents of MCTs that are considered functional lipids, since they are related to beneficial health effects (Alabdumkarim, Bakeet & Arzoo, 2012). Among the main benefits are the prevention and treatment of obesity, through increased thermogenesis, fat oxidation and energy expenditure (Nagao & Yanagita, 2010), increased

satiety and decreased food intake (Coleman, Quinn & Clegg, 2016) and antidiabetic properties (Nagao & Yanagita, 2010). Other dietary sources of MCTs include other lauric fats such as palm, palm kernel and coconut oils, cocoa butter and animal fats (Alabdumkarim, Bakeet & Arzoo, 2012).

3.3 FT-IR Analysis

The spectra obtained for the babassu kernel oil samples can be seen in Figure 1A. The spectra present two regions with different band intensities between the EVBO and the VBO. In both, an increase in the intensities for the VBO sample can be observed in the vibration range 3955 – 3420 cm^{-1} (Figure 1B). This result is possibly due to the higher content of hydroperoxides and free fatty acids resulting from the hot extraction process. This range of vibration is linked to the over-tone ester vibrations (−C=O) (Tena, Aparicio & García-González, 2017) and stretches peroxides (−OH) (Zahir, Saeed, Hameed & Yousuf, 2017). In the range 1700 – 1480 cm^{-1} the band is highlighted at 1664 cm^{-1} which is attributed to the presence of carbonyl groups (C=C) of unsaturated fatty acids that are slightly larger in the VBO.

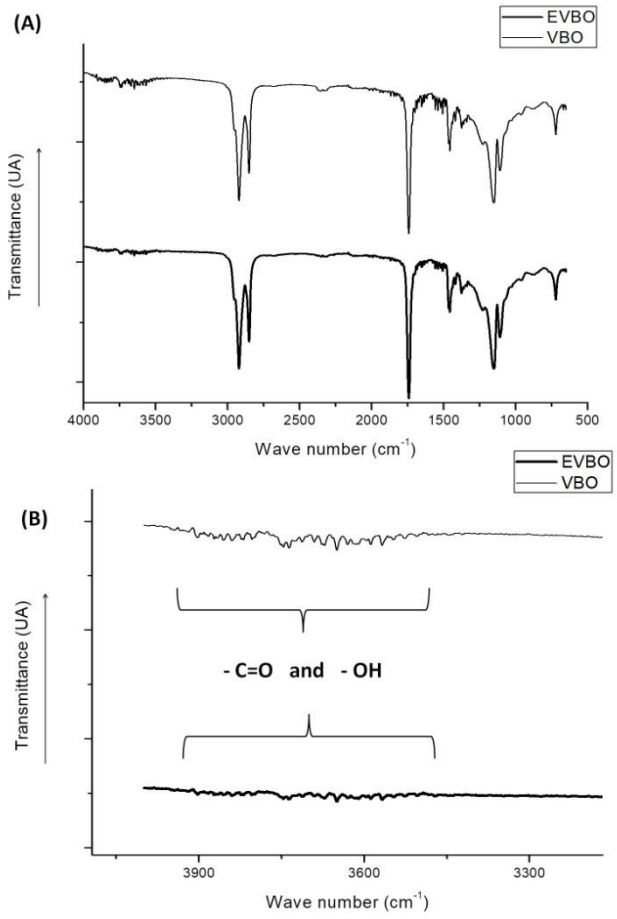

Figure 1. FT-IR spectra of babassu oil samples obtained by different extraction methods.

In addition, another 10 bands can be identified in the babassu oil spectra. The bands at 2920 cm^{-1}, 2850 cm^{-1}, 1457 cm^{-1} e 720 cm^{-1} are related as different vibrations of the $–CH_2$ group, an intensity depending on the size of the carbon chain of the fat acids (Sagiri et al., 2015). The bands present at 1745 cm^{-1}, in the range 1231-1152 cm^{-1} and 1664 cm^{-1} and 1231-1109 cm^{-1}, respectively, as vibrations modes at O–C=O, C–O and C=C–C–O in the head of the triacylglycerol esters (Sagiri et al., 2015), in this case, the lower carbon chain weights are the ones that suffer the highest incidence due to the increased polarity of the molecule when compared to the long chain triacylglycerols. In addition, as detected vibrations at 2955 cm^{-1} and 1380 cm^{-1}, they are linked as vibrations of CH_3 groups present in the triacylglycerol tails (Ferreira, Faza & Le Hyaric, 2012). These bands were also identified in the spectra obtained by Ferreira, Faza & Le Hyaric (2012) in a comparative study between indaia and babassu oils.

3.4 DSC Analysis

In Table 4 presents the data for the DSC analyses of the two types of babassu oil studied, extra virgin (EVBO) and virgin (VBO). The thermograms are shown in Figure S2 (a and b) in the Supplementary Material, respectively. Data shown as differences for enthalpies of crystallization and melting of the two oils. These differences are possibly due to the previous history of the materials, since the extra-virgin oil is obtained through a milder process than the virgin babassu oil. The latter is heated for a prolonged time which may change the conformation of its structures, in addition to the formation of compounds of shorter chains, as shown by the results of lipid profile and physical chemistry. This greater compound heterogeneity makes it difficult to pack and approach fatty acids in the VBO, which makes their molecular interactions weaker by decreasing the energies required for phase transition.

The thermograms of the crystallization (Fig. S2a) show the differences between the crystallization behavior of babassu oils. EVBO has two well-defined exothermic peaks. VBO has only one exothermic peak with a change in bending at 10.1°C and peak temperature at 4.9°C. For both oils the crystallization starts at approximately 11°C, but finishes at - 3.2 ° C for EVBO and -2.4 ° C for VBO. Unlike crystallization, the extraction method did not influence the melting behavior of the different babassu oils (Fig. S2b). Tan & Che Man (2002) in a study comparing palm, palmist and coconut oils obtained similar results for the melting temperatures of palmist (26.33 ° C) and coconut (22.45 ° C) oils. However, for the crystallization temperature, the same authors found values between 7.83 ° C (palmist oil) and -7.86 ° C (coconut oil), showing the

highest proportion of unsaturated fatty acids present in coconut oil, when compared to babassu or palm kernel oils.

Table 4. DSC analysis of crude babassu oil samples.

	Melting			
	T_{onset} (°C)	T_{peak} (°C)	T_{offset} (°C)	ΔH (J/g)
EVBO	13.33±0.23[a]	26.52±0.08[a]	32.84±0.20[a]	117.19±0.66[a]
VBO	13.07±0.07[a]	26.40±0.13[a]	32.10±0.84[a]	107.84±1.75[b]
	Crystallization			
	T_{onset} (°C)	T_{peak} (°C)	T_{offset} (°C)	ΔH (J/g)
EVBO	11.16±0.23[a]	10.13; 4.84[a]	-3.19±0.08[a]	85.98±1.23[a]
VBO	11.33±0.38[a]	10.14; 4.55[a]	-2.38±0.15[b]	80.19±0.97[b]

Results presented as means ± standard deviations. Results followed by different letters in the same column are significantly different by the F-test at 5% probability.

3.5 TGA Analysis

The data acquired in the TGA analysis of the babassu oil samples are represented in the TG and DTG curves in Figure 2 (a and b). These curves represent the thermal behavior of the oils, where the thermal stability is represented by the temperature range where the mass remains unchanged, that is, up to 165°C for EVBO and 125°C for VBO. The lower stability of the hot extracted oil may be related to its content of monoacylglycerols and higher values of acidity, peroxide index, dienes and trienes conjugated (Table 1). These data indicate that the oil decomposition process may have been initiated during the VBO acquisition step and are reflected in the thermogravimetric analysis.

The process of decomposing the samples occurred in two stages, the first in a wide temperature range and the second in the narrowest range. The first stage refers to the decomposition of oils (165°C – 415°C for EVBO and 125°C – 415°C for VBO) and the second stage to combustion and carbonization of the material (415°C – 450°C for both samples). In addition, a third step is observed in the range between 450 and 600°C, however these reactions did not represent detectable mass losses in the TG curves.

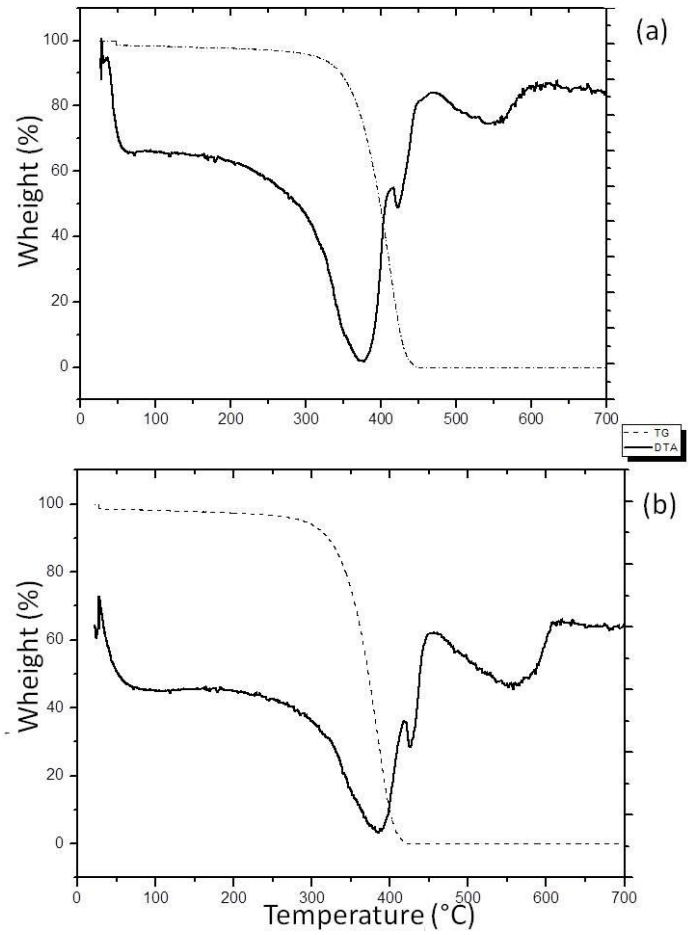

Figure 2. TG/DTA curves of the different babassu oils, EVBO (a) and VBO (b).

3.6 Content in Minerals

The type of extraction modified the content of minerals present in different babassu oils, EVBO and VBO. No amount of iron was detected in the samples. The only mineral detected in EVBO was phosphorus (0.37 ± 0.04 mg / kg). On the other hand, calcium (0.40 ± 0.05 mg / kg), magnesium (0.38 ± 0.05 mg / kg) and phosphorus (2.63 ± 0.24 mg / kg) were present in the VBO. The detected elements are of endogenous origin in the raw material. Naozuka, Vieira, Nascimento & Oliveira (2011), analyzing the mineral content in different fruits of Amazonia, including babassu, observed that the main minerals present in babassu kernels are potassium, phosphorus, magnesium, sulfur and calcium, iron concentrations and other low quantity elements.

A higher concentration of minerals is observed in the VBO. This result may be related to the extraction steps taken to obtain this type of oil. In the cooking step of the babassu kernel mass, a certain amount of water is added which favors the release of the minerals from the solid matrix and which consequently remain in the oil after the evaporation step.

The presence of traces of minerals in oils and fats may be endogenous to the raw material itself (animal or vegetable) or may originate during the processing steps, such as extraction or refining or due to corrosion of the equipment, or the presence of pesticide residues or contamination input through industrial water (Nosratpour & Jafari, 2018). In this context, the characterization of oils and fats, as to their trace element content, can serve as a basis for determining their nutritional and technological quality, such as purity, freshness and stability.

4 Conclusions

Babassu oil is an edible oil that can be easily produced and has a lipid composition similar to palm kernel and coconut oil, widely used as food. The results show that the type of extraction modifies the amounts of fatty acids in each babassu oil, but does not interfere with the types of fatty acids found in EVBO or VBO. Despite the differences found between the characteristics of different babassu oils, both EVBO and VBO can be considered products with good nutritional and technological quality. Its thermal and physical characteristics allow its use in different food products, such as chocolates, ice cream, margarines, creams and other confectionery and bakery products, as well as raw material for the manufacture of edible grade emulsifiers.

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Conflict of Interest

Not one.

Supplementary Material

Table S1. Thermal properties, density (ρ), viscosity (η) and interfacial tension oil/air and oil/water (ϒ), of different types of babassu oil as a function of temperature.

EVBO				
Temperature (°C)	ρ (kg / m³)	η (Pa.s)	ϒ (oil/air) (mN / m)	ϒ (oil/water) (mN / m)
30	915.041±0.003	0.036±0.001	28.333±0.047	11.700±0.141
40	907.901±0.002	0.024±0.000	27.750±0.071	11.800±0.071
50	900.808±0.006	0.018±0.000	27.117±0.024	11.900±0.141
60	893.765±0.005	0.013±0.000	26.367±0.094	12.050±0.047
70	886.757±0.009	0.010±0.000	25.700±0.047	12.100±0.071
80	879.777±0.008	0.008±0.000	25.033±0.047	12.150±0.000
VBO				
Temperature (°C)	ρ (kg / m³)	η (Pa.s)	ϒ (oil/air) (mN / m)	ϒ (oil/water) (mN / m)
30	915.413±0.007	0.038±0.000	28.367±0.047	11.800±0.071
40	908.295±0.007	0.025±0.000	27.750±0.071	11.900±0.212
50	901.221±0.001	0.018±0.000	27.167±0.047	11.950±0.212
60	894.195±0.001	0.013±0.000	26.500±0.000	12.000±0.141
70	887.202±0.003	0.010±0.000	25.900±0.000	12.100±0.000
80	880.237±0.008	0.008±0.000	25.167±0.000	12.200±0.000

Results presented as means ± standard deviations of the analyzes of each type of babassu oil.

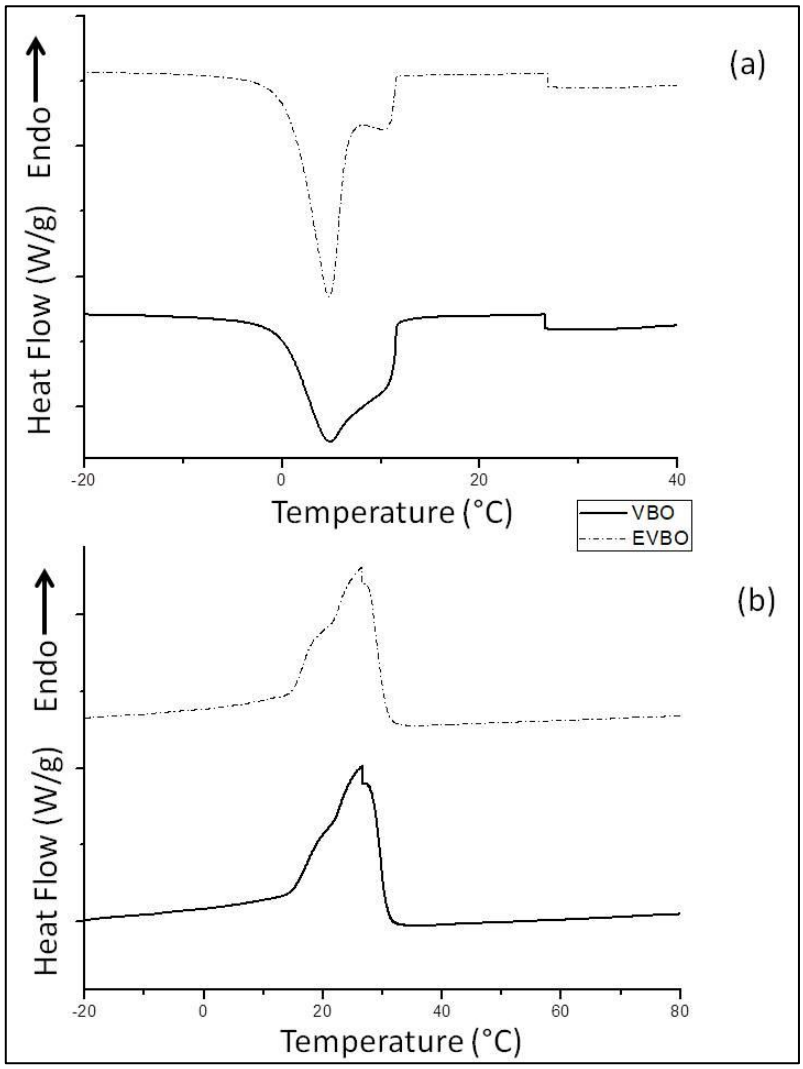

Figure S2. Thermograms of the crystallization (a) and melting (b) of different babassu oils.

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Capítulo 4

Artigo 2

ANTIOXIDANT ACTIVITY AND BIOACTIVE COMPOUNDS OF BABASSU (*Orbignya phalerata*) VIRGIN OIL OBTAINED BY DIFFERENT METHODS OF EXTRACTION

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ANTIOXIDANT ACTIVITY AND BIOACTIVE COMPOUNDS OF BABASSU (*Orbignya phalerata*) VIRGIN OIL OBTAINED BY DIFFERENT METHODS OF EXTRACTION

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Abstract:

Background: The investigation of new sources of raw materials and the knowledge of the composition of the food is fundamental for the evaluation of their potential and the availability of nutrients for the consumer population.

Objective: This work aimed to deepen the knowledge about the crude oil of babassu fruit obtained by two different methods of extraction, cold pressing and extraction by cooking the fruit almond.

Method: Total phenolic compounds contents and antioxidant activity were determined by ferric reducing antioxidant potential assay and 2,2-diphenyl-1- picrylhydrazyl radical scavenging capacity assay. By liquid chromatography, the content of different bioactive compounds was determined. Data was submitted to Analysis of Variance (ANOVA) and compared by f test ($p < 0.05$).

Results: The results showed that for most of the bioactive compounds there was no difference between the two types of babassu oil. For those compounds where the oils differed, the virgin oil had about three times the content of the extra-virgin oil. In addition, the antioxidant activity was higher for the oil extracted by cooking of the babassu mass, ranging from approximately 2.5

times higher up to 19.2 times higher than the antioxidant activity of the babassu oil extracted by pressing.

Conclusion: The process of extraction by cooking the almond mass can incorporate a larger number of bioactive components and improve the antioxidant activity of the virgin babassu oil. However, the extraction method does not influence the content of tocopherols of distinct types of babassu oil.

Keywords: *Orbignya phalerata*, Phenolic compounds, Tocopherols, FRAP, DPPH, Liquid chromatography.

1 Introduction

Vegetable oils are those obtained from parts of plants, such as seeds, nuts, flowers and fruit pulp, vegetables and legumes mainly formed by lipids. They are the most produced and consumed oils in the world [1] and represent significant importance in the population's diet. They are sources of saturated and unsaturated fatty acids, liposoluble vitamins and antioxidants [2, 3].

Vegetable oils are versatile raw materials for the food, pharmaceutical and chemical industries, as they have different compositions and technological uses [3, 4]. For example, oils from oilseeds are rich in polyunsaturated fatty acids and vitamins [3, 5, 6], fruit pulp oils such as oil palm and olive oil have a high amount of antioxidant compounds [7, 8, 9] and palm kernel oil have a large amount of saturated fatty acids [10, 11]. These different compositions allow vegetable oils to be applied to various products. In the food industry they are used to cook or fry [12, 13], as ingredients of different food products, creams and margarines [14, 15, 16], bakery products [17], ice cream [18], chocolates [19]. In the pharmaceutical industry these oils are used in cosmetics [20, 21] and therapeutic formulations [22, 23].

Thus, the world demand for oils and fats is increasing, so several researchers are engaged in finding new sources of vegetable oils with high nutritional quality, industrial importance and pharmaceutical activity [24 – 31]. Brazil has a great biodiversity and therefore an infinity of plants potentially producing oil, among them the babassu.

Babassu (*Orbignya phalerata Mart.*) is a palm commonly found in the North and Northeast regions of Brazil [32]. Babassu is a valuable resource in these regions both in economic and nutritional terms [33]. This importance is related to the exploitation of the culture [34], which is extractive and exploited by low-income people, as well as the substantial number

of products and by-products that can be originated using this fruit. Babassu oil is the main product, usually used in the diet of the population of these regions [10, 32, 34] or for the production of cosmetics and hygiene and cleaning products [35, 36], and, also for the production of biofuels [36, 37, 38], being the by-products destined for other uses, such as the use of the deffated cake for animal feed [34, 39, 40].

According to Carazza *et al.* (2012), there are basically two forms of processing to obtain babassu oil, both handmade in domestic or cooperative form. One process is performed by cold mechanical pressing and in the other, by cooking the mass of babassu crushed almonds. Extra-virgin babassu oil is obtained by cold pressing whole, healthy almonds without yellowing or superficial physical damage, followed by decantation, filtration and packaging. The virgin babassu oil is obtained by crushing previously selected and toasted almonds, followed by baking the mass to obtain the oil, which is separated by decanting, filtered and reheated for total removal of the water resulting from the cooking step and then packaged.

Babassu oil is composed mainly of saturated fatty acids (80-91%), such as lauric acid (43-50%), myristic acid (15-18%), palmitic acid (6-10%), capric acid (4-6%), caprylic acid (0-5%) and stearic acid (3-5%); the remainder are unsaturated fatty acids (9-20%), where oleic acid (12-19%) and linoleic acid (1-3%) are present [10, 38, 41]. This composition is like that of palm and coconut oils, and has already been reported in the literature [42, 43, 44].

Currently, babassu oil is less used in the food industry, its major use is in the personal care industry, in the manufacture of surfactants, soaps and cosmetics in general. This is mainly because babassu oil has a high capacity to form soaps and possesses high emollient power [45]. To obtain information that may stimulate other applications of this native Brazilian raw material, the objective of this study was to investigate the content of bioactive compounds and the antioxidant activity of different types of crude babassu oil obtained employing the two most used forms of extraction.

2 Material and Methods

2.1 Samples

The samples of babassu oil were obtained directly from producers in the states of Tocantins and Maranhão, Brazil. Extra-virgin babassu oil (EVBO) was obtained by cold pressing whole, healthy almonds without yellowing or superficial physical damage, followed by decantation, filtration and packaging. The virgin babassu oil (VBO) was obtained by crushing previously selected and toasted almonds, followed by baking the mass to obtain the oil, which

was separated by decanting, filtered and reheated for total removal of the water resulting from the cooking step and then packaged.

2.2 Chemical Reagents

During the experiments, the following solvents and reagents were used: methanol with purity > 99% (Ecibra, Santo Amaro, São Paulo, Brazil) hexane with purity 98.5% (Synth, Diadema, São Paulo, Brazil), ferric chloride hexahydrate with purity 97% (Sigma-Aldrich, Sant Louis, USA) and ferrous sulfate heptahydrate with purity ≥ 99% (Sigma-Aldrich, Sant Louis, USA). Acetonitrile, methanol, hexane, isopropanol and acetic acid (Sigma-Aldrich, Sant Louis, USA) (both of whit purity ≥ 99.9%). Deionized water (deionizer Marte Científica, Santa Rita do Sapucaí, Minas Gerais, Brazil) and ultrapure water (Ultra water purifier MS2000, Gehaka, São Paulo, Bazil).

Folin-Ciocalteau reagents, DPPH radical solution (2,2_-diphenyl-1-picrylhydrazyl), TPTZ (2,4,6-Tris (2-pyridyl) -s-triazine), all from Sigma-Aldrich (Sant Louis, USA) were used for the analysis of antioxidant activity.

The analytical standards for the chromatographic analyzes were: gallic whit purity ≥ 99.9%, caffeic acid whit purity ≥ 98%, catechin whit purity ≥ 99%, quercetin with purity ≥ 99%, rutin with purity ≥ 96%, α-tocopherol with purity ≥ 96%, β-tocopherol, γ-tocopherol with purity ≥ 96% and δ-tocopherol with purity ≥ 96%, lycopene with purity ≥ 95%, β-carotene with purity ≥ 97% and α-carotene with purity ≥ 95%, all from Sigma-Aldrich (Sant Louis, USA).

2.3 Methods

2.3.1 Antioxidant Activity and Bioactive Compound Content Assays

The analyzes of antioxidant capacity and phenolic compound content of crude babassu oils (EVBO and VBO) were carried out from the methanolic extracts, as explained below, of the samples. The quantification of tocopherols and carotenoids was performed directly for the samples of the oils.

2.3.1.1 Obtention of the methanolic extracts of crude babassu oil samples

The extracts were obtained according to the procedure described by Montedoro *et al.* [46]. Approximately 5.0 g of each type of oil were mixed with 1.0 mL of methanol/water

solution (80:20 v/v) and vortexed for 2 min. This mixture was centrifuged at 1080g for 10 min and the methanolic portion was collected. These steps were repeated 3 more times and the supernatants were combined to form the extract.

2.3.1.2 Antioxidant Activity Assays

The total phenolic compounds of the samples [47] were determined using the Folin-Ciocalteau reagent (FCR) and solutions of gallic acid with different concentrations for the construction of the analytical curve, ranging from 0.01 to 0.1 mg/mL. 0.2 mL aliquots of the methanolic extracts were mixed at 0.2 mL of FCR. After 4 min, 1.6 mL of 5% (m/v) calcium carbonate aqueous solution was added. The mixture remained 20 min in thermostated bath at 40°C and then the assays were monitored on a Shimadzu UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan). The absorbance was measured at 750 nm against a blank which was methanol. The total content of phenolic compounds in the extracts was expressed in mg of gallic acid equivalent per 100 g of babassu oil.

The antiradical activity of the oils was measured using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical following the procedure described by Franco *et al*. (2014). Aliquots of 0.1 mL of methanolic solution of the babassu oil extracts (4 different concentrations) were mixed with 3.9 mL of the 60 μM DPPH solution. These mixtures were held in the dark for 30 min and then the absorbance was measured at 515 nm against a blank which was methanol. The percentage of inhibition of the radical was calculated according to Equation 1 and these results were used to obtain a curve relating the percentage of inhibition of the radical versus the concentration of the extract. Through linear regression the IC_{50} was calculated which is the value that estimates the antioxidant concentration required to inhibit 50% of the DPPH radical.

$$\%\ Inhibit\ DPPH\ = \frac{Abs_{DPPH} - Abs_{Sample}}{Abs_{DPPH}} \times 100 \qquad (1)$$

Where:

Abs_{DPPH} is the measured absorbance for the solution containing only the radical DPPH (UA);

Abs_{Sample} is the absorbance measured after the reaction between the extracts of the samples and the radical DPPH (UA).

Antioxidant activity using the ferric reducing method (FRAP) was evaluated as described by Benzie & Strain [49], with some modifications. Aliquots of 0.9 mL of the methanolic extracts of babassu oils, plus 0.27 mL of distilled water and 2.7 mL of the FRAP reagent were homogenized and incubated at 37° C for 30 minutes. After this period a reading at 595 nm was carried. To obtain the analytical curve, the same procedure was repeated by replacing the aliquots of extract by ferrous sulfate solutions with different concentrations ranging from 0.15 mM to 5 mM. Thus, the results were expressed in mmol of ferrous sulphate/g of babassu oil.

2.3.1.3 Contents of Bioactive Compounds

2.3.1.3.1 Phenolic Compounds

The presence of different phenolic acids and flavonoids, namely gallic acid, caffeic acid, catechin, quercitin and rutin, were investigated. For the identification and quantification of these bioactive compounds, the methanolic extracts of the EVBO and VBO samples were obtained as described previously in item 2.3.1.1. These extracts were purified by the procedure also described by Montedoro *et al*. [46]. The methanolic extract was rotoevaporated at 30° C until complete evaporation of the solvent, and then resuspended in 1.0 mL of acetonitrile. This solution was washed three times with 1.0 mL of hexane and the acetonitrile layer was separated and evaporated at 30° C. The resulting residue was dissolved in 1.0 mL of chromatographic grade methanol and filtered through a 0.45 μm pore syringe filter.

The analyzes were performed using a liquid chromatograph (Shimadzu, Kyoto, Japan), equipped with a quaternary pump system, degasser, injection valve with 20 μL sampling loop, column furnace and diode arrangement detector. The phenolic compounds were separated on C18 reverse phase analytical column (0.25 m x 4.6 mm d.i. x 5μm particle size) (Supelco Analytical, Bellefonte, USA).

The operating parameters of the chromatograph were established as described by Azevedo *et al*. [50]. The mobile phase consisted of a mixture of two solvents, acidified water (98: 2 v/v acetic acid water) (Solvent A) and methanol (Solvent B). Elution occurred in a gradient ranging from 100% A to 50% A and 50% B in 5 min. Passing to 35% A and 65% B in 7 min and remaining in this proportion up to 10 min. Between 10 and 12 min returning the condition 50% A and 50% B and passing to 100% A in 15 min, thus remaining up to 18 min for column stabilization and preparation for a new run. The mobile phase flow was adjusted to 1.0 mL / min and the column furnace temperature remained at 40 ° C throughout the run.

Identification of the phenolic compounds was performed by comparing the peak retention time of the samples with the peak retention time of gallic acid, caffeic acid, catechin, quercetin and rutin and by the characteristic wavelength of each substance. Chromatograms were processed at 280 nm for gallic acid and catechin, 330 nm for caffeic acid and 360 nm for quercitin and rutin [50].

The quantification of the phenolic compounds was done through external standardization. The analytical curves were constructed by injecting solutions of the standards with concentrations ranging from 0.2 x 10^{-3} to 0.2 μg/mL and the phenolic amounts present in the EVBO and VBO were calculated using the equations of the lines.

2.3.1.3.2 Tocopherols and Carotenoids

The presence of non-esterified tocopherols and carotenoids was investigated. For identification and quantification of these compounds, 0.05 g of each of the oils were weighed and 950 μl of HPLC grade hexane was added. The mixture was run on a vortex type stirrer (Labnet International Inc., Edison, New Jersey, EUA) for 30 seconds and centrifuged in the microcentrifuge MiniStar (VWR Colletion, Vienna, Austria) at 1080g for 5 min. The supernatant was collected and filtered through a 0.45 μm pore diameter syringe filter [51].

The analyzes were performed using a Shimadzu liquid chromatograph (Kyoto, Japan), equipped with a quaternary pump system, degasser, injection valve with 20 μL sampling loop, column furnace and diode arrangement detectors and fluorescence. The analytes were separated on Zorbax-SIL normal phase analytical column (0.25 m x 4.6 mm d.i. x 5μm particle size) (Supelco Analytical, Bellefonte, USA).

The mobile phase consisted of a mixture of hexane: isopropanol (99:1, v / v), elution being isocratic. The mobile phase flow was adjusted to 1.0 mL / min and the column furnace temperature remained at 25 ° C throughout the run [52].

The identification of the compounds was performed by comparing the sample retention time with the peak retention time of the carotenoid standards (lycopene, β-carotene and α-carotene) and tocopherols (α, β, γ and δ- tocopherols) and also by the characteristic wavelength of each substance. Chromatograms were processed at 290 nm (excitation) and 330 nm (emission) at the fluorescence detector for the tocopherols; and, between 390 and 700 nm, in scan mode, in the diode arrangement detector for carotenoids [53, 54].

The quantification of tocopherols was done through external standardization. The analytical curves were constructed by injecting solutions of the standards with concentrations ranging from 0.01 to 1.5 μg / mL. The amounts of these compounds present in EVBO and VBO

were calculated using the equations of the lines obtained for each curve. Curves were not constructed for carotenoids because they were not detected in the samples.

2.3.2 Statistical Analysis

The data obtained in this study, both for the antioxidant activity and for the content of bioactive compounds, was submitted to analysis of variance (ANOVA) using the SAS program, Studio version.

The antioxidant activity and contents of the different phenolic compounds and tocopherols were expressed as mean ± standard deviation and were compared using the f test ($p < 0.05$).

3 Results

3.1 Antioxidant Activity

The determination of the antioxidant capacity is based mainly on two mechanisms of reaction, the transfer of a hydrogen atom and / or the transfer of an electron. In addition to the mechanism, the objective is to determine the protective effect of the material against free radicals, which differ in the initiator radical, reaction kinetics and side reactions [55]. Thus in investigating the total antioxidant capacity of a substance it is important that at least one test of each mechanism is used. Thus, the samples were tested for the DPPH radioactivity and ferric reducing antioxidant potential assay (FRAP). In the DPPH assay both mechanisms are involved and in the FRAP assay the transfer of a hydrogen atom is involved [56, 57, 58].

The results for the determinations of the antioxidant activity of the different babassu oils studied (EVBO and VBO) can be observed in Table 1. Regardless of the test used, the antioxidant activity was higher for the oil extracted by cooking the babassu mass, ranging from ≈ 9.3 times higher up to 19.7 times higher than for the antioxidant activity of the extra virgin babassu oil.

Table 1. Antioxidant activity of babassu crude oils obtained by different extraction methods.

Antioxidant Assay	Type of Babassu Oil	
	EVBO	VBO

Total Phenolic (FCR) (mg gallic acid / g oil)	$1.1^{a} \pm 0.1$	$22^{b} \pm 2$
Ferric Reducing Test (FRAP) (mM ferrous sulfate / g oil)	$0.3^{a} \pm 0.3$	$2.8^{b} \pm 0.2$
DPPH radical assay (IC_{50}) (mg / mL)	$2349^{a} \pm 57$	$121.5^{b} \pm 0.8$

Results presented as means ± standard deviations of the analyzes of each type of babassu oil. Results followed by different letters in the same line are significantly different by the f test at 5% probability.

3.2 Contents of Bioactive Compounds

Chromatographic conditions were suitable for separating the different phenolic compounds, gallic acid, caffeic acid, catechin, quercetin and rutin (Figure 1) and tocopherols (α, β, γ, and δ-tocopherol) (Figure 2) present in the babassu oil samples.

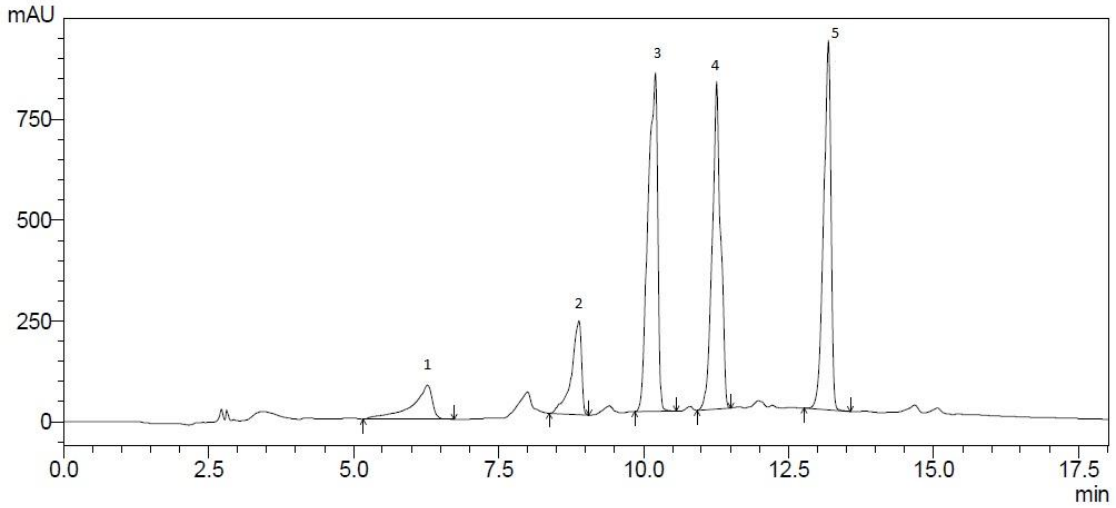

Figure 1 – Chromatogram characteristic of babassu oil samples. Separation of different phenolic compounds: 1) Gallic acid; 2) Catechin; 3) Caffeic acid; 4) Rutin; 5) Quercitina.

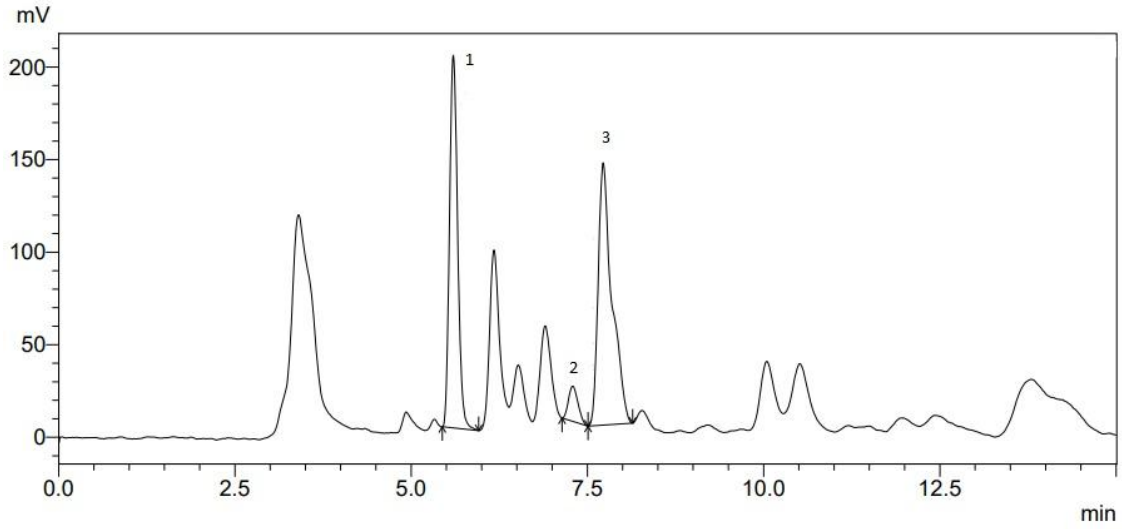

Figure 2 – Chromatogram characteristic of babassu oil samples. Separation of the different tocopherols: 1) α-tocopherol, 2) β-tocopherol and 3) γ-tocopherol.

The results for the quantification of the bioactive compounds, phenolics, tocopherols and carotenoids in the different babassu oils (EVBO and VBO) can be observed in Table 2. For most of the compounds there was no difference between the types of oil. In cases where the oils differed, VBO presented content about three times higher than EVBO, except for gallic acid, where this ratio was reversed. With regard to catechin, it can be observed that for the EVBO samples the presented values are low and with high variability. Thus, the presence of this compound can be confirmed, but it is not possible to determine in what quantities.

Table 2. Content of the bioactive compounds identified in the different types of crude babassu oils.

Compounds Bioactive (mg / 100g of oil)	Type of crude babassu oil	
	EVBO	VBO
Gallic acid	$0.17^{a} \pm 0.02$	$0.06^{b} \pm 0.03$
Caffeic Acid	$0.045^{a} \pm 0.001$	$0.111^{b} \pm 0.003$
Catechin	$0.03^{a} \pm 0.02$	$0.72^{b} \pm 0.02$
Quercitin	$0.21^{a} \pm 0.01$	$0.23^{a} \pm 0.01$
Rutin	$0.18^{a} \pm 0.02$	$0.13^{a} \pm 0.01$

α-tocopherol	1.61[a] ± 0.08	1.32[a] ± 0.03
β-tocopherol	3.50[a] ± 0.08	3.46[a] ± 0.03
γ-tocopherol	1.45[a] ± 0.07	1.61[a] ± 0.06
δ-tocopherols	Not detected	Not detected
Carotenoids	Not detected	Not detected

Results presented as means ± standard deviations of the analyzes of each type of babassu oil. Results followed by different letters in the same line are significantly different by the test f at 5% probability.

4 Discussion

4.1 Antioxidant Activity

Analyzes for concentrations of total phenolic compounds showed a significant difference between the types of babassu oil studied. Phenolic compounds are substances that have structures with aromatic rings and double conjugated bonds from which they exert their antioxidant action, besides being the most abundant antioxidants in the diet [59]. They are generally determined via reaction with the Folin-Ciocalteau reagent. However, this reagent is not only sensitive to phenolic compounds [60]. Other structures with reducing power may also influence the results, for example of conjugated aldehydes, ketones, dienes and trienes, in addition to the melanoidins.

The process of obtaining VBO has two important stages of heating. At first, the mass of crushed kernel is cooked with a little water for oil scoring, which by being less dense floats on the cake and can be separated. In the second stage, this oil collected, still has a certain amount of water and therefore goes through an evaporation process. Thus, this exposure to heat may have favored oxidation and darkening reactions and consequently raised the total phenolic values of virgin babassu oil.

The oxidation of fatty acids leads to the formation of compounds such as aldehydes, ketones, dienes and conjugated trienes, among others [61]. And melanoidins are heterogeneous brown pigments that have aromatic rings, are formed by reactions of non-enzymatic browning [62, 63]. These pigments are produced during the Maillard reaction. This reaction occurs between the carbonyl groups of reducing sugars and the amino groups of amino acids, peptides or proteins, and is catalyzed by heating [64, 65]. The presence of proteins and carbohydrates in the babassu cake [66] together with the heating during the VBO extraction process contribute to

the formation of these compounds.

Regarding antioxidant capacity, both types of babassu oils can be considered low antioxidant power. Ferreira et al. (2011) evaluating the antioxidant capacity of different oils, including babassu oil, obtained comparable results. Essential oils such as oregano and thyme, which have high antioxidant capacity, have values between IC50 3.9 and 1.1 mg / mL [67]. When compared with excellent antioxidant substances, such as ascorbic acid and BHT [68], babassu oil presents activity up to 11.11 x 10^5 times lower. This may be related to the plant's own anatomy. The babassu kernel is protected within the fruit by at least three layers, epicarp, mesocarp, and endocarp [32, 34, 70] that form a protective physical barrier for the constituent substances of this almond, so the plant need not produce other compounds for this purpose.

4.2 Contents of Bioactive Compounds

The differences presented by EVBO and VBO oils, both for the antioxidant activity discussed above and the content of phenolic compounds may be related to the higher release of these bioactive substances from the food matrix when it is heated. The presence of water in the cooking step increases the solubility of flavonoids and phenolic acids, consequently increasing their extraction during the process. With the evaporation of water these components remain in the extracted oil. Equivalent results were demonstrated by Serevinatne *et al*. (2008) in a study about the influence of the method of coconut oil extraction on the content of phenolic compounds of this product.

Generally flavonoids, among them, catechin, quercetin and rutin, are the predominant class among the phenolics present in plant foods. However, the presence of phenolic acids, such as gallic and caffeic acids, is considered beneficial since these compounds are considered multipurpose bioactive. These acids, in addition to the known antioxidant effect, may still have antimutagenic, anticarcinogenic, anti-inflammatory and antimicrobial action [59, 72].

The tocopherols are part of the compounds with vitamin E activity and are the main antioxidants naturally present in vegetable oils [51]. The biological activity varies among the isomers, with an increased vitamin activity associated with greater methylation and heightened activity associated with methylation at the fifth carbon, vitamin activity: $\alpha > \beta > \gamma > \delta$ [6, 73, 74]. According to the Specified Oil Standard [73] babassu oil has low or undetectable levels of these compounds. The results presented in this study show low levels of total tocopherols ($\cong$ 6.5 mg / 100 g of olive oil), and not all of them are found. This fact may be related to the fatty acid composition of babassu oil. Since babassu oil is mostly composed of saturated fatty acids and is therefore more stable, a high concentration of these natural antioxidants is not expected. Other

highly saturated vegetable oils, such as coconut oil and palm kernel oil, also have low or undetectable levels of tocopherols [73]. On the other hand, in more unsaturated vegetable oils have highly levels of tocopherols, such as palm (≅ 19 mg / 100 g oil) [76], soybean oil (≅ 40 mg / 100g oil) [77], canola (≅ 65 mg / 100g oil) [78], sunflower (≅ 80 mg / 100g oil) [51] and olive oil (200-450 mg / 100g olive oil) [79].

5 Conclusion

The results obtained demonstrate that the extraction method can influence the characteristics and composition of crude babassu oil. Extraction by cooking the crushed kernel cake is capable of incorporating a larger amount of bioactive compounds. This process improves the antioxidant capacity of virgin oil (VBO). Despite this, regardless of the method chosen for its production, babassu oil can not be considered a potential source of antioxidants.

6 List of Abbreviations

DPPH – 2,2-diphenyl-1-picrylhydrazyl
EVBO – Extra-Virgin Babassu Oil
FCR – Folin-Ciocalteau Reagent
FRAP – Ferric Reducing Antioxidant Potential
HPLC – High Performance Liquid Chromatography
VBO – Virgin Babassu Oil

7 Conflict of Interests

The authors confirm that the content of the article has no conflict of interest.

8 Acknowledgment

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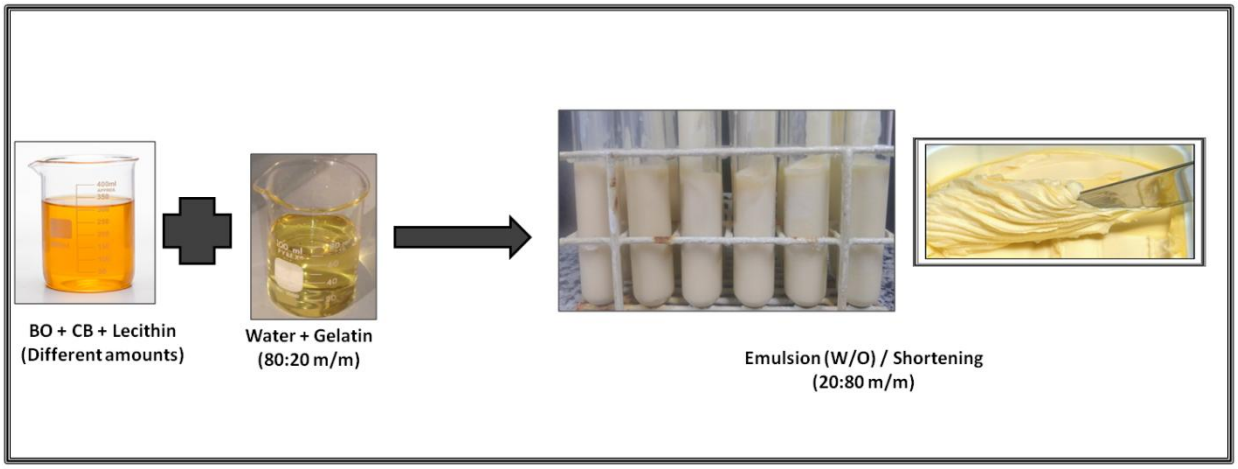
Capítulo 5

Artigo 3

WATER-IN-OIL EMULSIONS CONSISTING OF BABASSU OIL, COCOA BUTTER AND GELATINE SOLUTION: FORMULATION AND CHARACTERISATION

Artigo será submetido ao periódico “Journal of Industrial and Engineering Chemistry”.

GRAPHICAL ABSTRACT



WATER-IN-OIL EMULSIONS CONSISTING OF BABASSU OIL, COCOA BUTTER AND GELATINE SOLUTION: FORMULATION AND CHARACTERISATION

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Abstract

The objective of this research was the formulation and characterization of water-in-oil (W/O) emulsions (20:80 m/m) containing different amounts of babassu oil and cocoa butter as continuous phase and gelatin solution (20% m/m) as dispersed phase. The emulsions were prepared by the hot method and six different emulsions containing only babassu oil were formulated until completely replaced by cocoa butter in the fat phase. Emulsions were evaluated for pH, conductivity, particle size, polymorphism, melt profile, FTIR-ATR analysis, hardness, spreadability and stability. The results showed that the stability (lower creaming formation, 24-0 %) and hardness (19-54 N) of the emulsions rose with the increase in the amount of cocoa butter in the formulations and was mainly related to crystallization of lipids. However, all emulsions showed good stability at 20°C or at cooling temperature and can be applied in different food products as a substitute for margarine or other vegetable shortenings.

Keywords: Orbignya phalerata Mart., *Theobroma cacao L.*, vegetable fat, colloidal systems, food industry, cosmetics industry.

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1. Introduction

The demand for oils and fats for food and pharmaceutical products has been increasing steadily due to the rapid growth of the population, the improvement in living standards and the change in consumer habits, both with personal care and food [1]. Generally, as different products are mixtures of ingredients, oils and fats are present in the form of emulsions, with W/O emulsions being widely applied in various products, such as in lipsticks, creams and lotions [2, 3], in pharmaceutical products, through the encapsulation and distribution of drugs [4] and in food products such as breads, cakes, cookies, pasta, fillings and toppings, ice cream, sauces, among others [5, 6, 7, 8].

Currently, W/O emulsions contribute to the desirable structural, sensory and nutritional characteristics of many processed food products [9, 10] are also used as a strategy to reduce the fat content [11, 12], to encapsulate bioactive compounds, mainly protection of hydrophilic compounds, and to control the release of different encapsulated compounds [13, 14], such as antioxidants [15, 16], vitamins [17], amino acids [18], minerals [19] and probiotics [20] among others.

The nature of the ingredients of an emulsion is closely linked to the stability of the system. The possible molecular interactions in each type of fat depend very much on their organization in triacylglycerols. In general, the main interactions of lipids are the attraction of van der Waals and steric repulsion and the strength of these interactions depends on the size of the fatty acid chains, degree of saturation or unsaturation and also symmetry of the triacylglycerol molecule. Longer chain fatty acids, saturated and symmetrically organized are more nonpolar and therefore the emulsion tends to be less stable than when the oil in the emulsion is made up of shorter or unsaturated acyl chains [21]. In addition, the presence of minor compounds such as mono and diacylglycerols, free fatty acids, phospholipids and polar antioxidants favors the stabilization of the system.

In this context, the discovery of new sources of oils and fats and the study of their influence on the formation and properties of emulsions is important for the industry. Babassu oil can be an interesting alternative, it is the product extracted from the coconut almonds of the babassu palm (*Orbignya phalerata Mart.*), An endemic plant in the Amazon rainforest of South America, especially Bolivia, Peru, Colombia and Brazil [22]. This oil is widely consumed as food in the North and Northeast regions of Brazil and is widely used by the pharmaceutical and cosmetic industry throughout the world, however still little used in processed foods, so much so that, to date, there is no research describing its use. as an ingredient for the food industry.

The lipid profile of babassu oil indicates that it can be an interesting alternative for the production of emulsions and other lipid bases, since it has the desirable characteristics for this purpose, such as short and medium unsaturated fatty acids, asymmetric triacylglycerols, in addition to different minority components [23, 24]. Babassu oil is mainly composed of lauric acid (43 - 50%), myristic acid (15 - 18%), oleic acid (12 - 19%), palmitic acid (6 - 10%), capric acid (4 - 6 %), caprylic acid (0 - 5%), stearic acid (3 - 5%) and linoleic acid (1 - 3%) [24 - 26]. In addition, its topical use or ingestion has some physiological benefits, such as antimicrobial effects, immunomodulatory effects and improvement of clinical symptoms, especially those linked to diseases such as cancer [27 - 29]. These benefits are attributed to its large amount of lauric acid, which is a fatty acid that has these therapeutic properties [30, 31] and also to the presence of unsaturated acids such as oleic and linoleic [29].

Babassu oil has physicochemical characteristics similar to palm kernel and coconut oils. Its crystallization and melting temperatures [24], related to the consistency and melting of lipids, suggest that babassu oil may be suitable to replace, at least partially, cocoa butter in different products [32]. In addition to being a more advantageous source of oil, as it is produced in a sustainable extractive manner (cleaner production), it contributes to the social and economic development of the collectors and still has a lower cost than cocoa butter.

Cocoa butter is extracted from Theobroma cacao L. almonds and is considered a unique fat, and its demand is expected to increase a lot in the coming years [32]. It has been widely used in foods (chocolates and confectionery), pharmaceuticals and cosmetics [33], mainly due to its physical characteristics, where it remains solid at room temperature and melts at body temperature. Due to its wide variety of applications and its unique properties, the availability of cocoa butter in large quantities has become a concern at the industrial level. Therefore, to meet this demand, work has been carried out to find alternatives to this source of vegetable fat [33 - 39].

In this context, the objective of this study was the development and characterization, physical, mechanical and stability, of water-in-oil emulsions for future applications as lipid bases in different products, such as food and cosmetics, among others. The emulsions were composed of different proportions of babassu oil and cocoa butter, in the continuous phase, and gelatin solution as a dispersed phase, being stabilized by an emulsifier which was lecithin.

2. Experimental

2.1 Materials

The babassu oil was supplied by producers in the state of Maranhão, Brazil. The cocoa butter was purchased from Barry Callebbaut Brazil (Bahia, Brazil). Soy lecithin was purchased from Tradal Brazil Ind. Com. LTDA (São Paulo, Brazil). Gelatin powder, brand Dr.Oetker, was acquired in the local commerce. Deionized water (Deionizer Marte Científica, Brazil) was used to produce the emulsions in this study.

2.2 Methods

2.2.1 Preparation of Emulsions

Six emulsions were prepared (Table 1), the proportions of each component were defined based on a previous study proposed by Sagiri et al. [34]. The fatty portion of each of the emulsions consisted of different proportions of the mixture of babassu oil (BO) and cocoa butter (CB) plus soy lecithin (3% w/w fat). The aqueous portion consisted of a 20% water gelatin solution (w/w, 60 °C).

The emulsions were prepared by the hot emulsification method [40] with some modifications. After weighing, the babassu oil, cocoa butter and soy lecithin were melted at 60°C and homogenized for 5 min at 500 rpm using a magnetic stirrer (Labnet International Inc., USA). The gelatine solution was added drop by drop to the fat mixture and homogenized for a further 15 min at 7000 rpm in an ultra-turrax homogenizer (GE 700 Basic, Metabo, Germany). The emulsion was packaged in 25 mL flasks and incubated at refrigeration temperature (4°C±1) for 24h to induce the gelatinization of the dispersed phase, fat crystallization and emulsion stabilization.

Table 1. Formulation of the different emulsions ($g_{component}$ / $100g_{emulsion}$)

Formulation	CB	BO	Water	Gelatine	Lecithin
A	77.6	00.00	16.00	4.00	2.40
B	62.08	15.52	16.00	4.00	2.40
C	46.56	31.04	16.00	4.00	2.40
D	31.04	46.56	16.00	4.00	2.40
E	15.52	62.08	16.00	4.00	2.40
F	00.00	77.6	16.00	4.00	2.40

CB – cocoa butter; BO – babassu oil.

2.2.2 Physical-chemical Analysis

Immediately after the preparation of the emulsions, before the refrigerated and gelatinization stage, the formulations were evaluated for their pH and electrical conductivity and particle size. The pH of each emulsion was determined using a benchtop potentiometer Quimis Q400MT (Quimis, Brazil). The electrical conductivity of the emulsions was measured using a Q795m digital conductivimeter (Quimis, Brazil).

2.2.3 FT-IR Analysis

The spectra of each emulsion were obtained through FTIR-ATR - Fourier Transform Infrared by means of Total Attenuated Reflection, in Agilent Cary® 630 equipment (Agilent, United States), under the middle infrared range, with the wavelength range of 4000 to 600 cm^{-1}, with resolution of 4 cm^{-1}, 64 scans and reading through the ATR diamond crystal.

2.2.4 DRX Analysis

The structural organization of emulsions was evaluated by means of X-ray diffraction. A D2 Phaser diffractometer (Bruker, Germany) was used to study the polymorphism of emulsions. The X-rays (ʎ = 1.54184 Å) were generated by a source Cu Kα. Diffraction was measured in the range 2θ of 5-50°.

2.2.5 Thermal Analysis

Thermal analyzes of raw materials and emulsions were performed on STA PT-1000 equipment (Linseis, Germany). Approximately 20 mg of each sample was placed in an open porcelain crucible under a static atmosphere of air and heated at a rate of 2°C / min.

For thermogravimetric analyzes (TGA), CB, BO, gelatin solution and emulsion C were heated from room temperature (≈ 25°C) to 800°C and thermograms were recorded allowing the evaluation of the thermal behavior of different materials.

For DSC analyzes, the emulsions were heated from room temperature (≈ 20°C) to 120°C, thermograms were acquired and the enthalpies of the phase transition of each formulation were determined.

2.2.6 Mechanical Analysis

2.2.6.1 Mechanical Properties

To evaluate the mechanical properties the emulsions were prepared (Item 2.2.1) and packed in cube-shaped bottles (22 mm edge). The hardness of each sample were sized using a pre-calibrated TA.HD plus texture analyzer (Stable Micro Systems, UK) equipped with a 50 kg load cell and a 100 mm diameter compression plate, probe (P/100). The samples were examined by uniaxial compression at a constant speed rate of 1.0 mm/s. All measurements were taken at cooling temperature (4 ± 1°C) and in three repetitions.

2.2.6.2 Spreadability

The spreadability of emulsions was calculated according to the method reported by Barakat [40]. The emulsions were stabilized at 20°C and 0.2 g of each formulation was placed between two glass slides of equal weight and area. Subsequently, known weights of 25 g, 50 g, 100 g, and 200 g were placed on the upper slide for a period of 30 s each. The initial and final scattering diameters were measured, respectively before and after the placement of the weight load, and the scattering of the emulsions was expressed as percentage (%) of scattering according to Eq. (1):

$$\%\ of\ Spreadability\ = \frac{d_2}{d_1} \times 100 \quad (1)$$

Where: d_1 is the initial diameter and d_2 is the final diameter.

2.2.7 Stability

The emulsions were stored refrigerated (4 ± 2°C), at 20 ± 0.5°C and room temperature (25 ± 2°C). At each 7-day period (0, 7, 14, 21, 28 days), each emulsion was evaluated for cracking and creaming index. Additionally, an accelerated thermal stability test was performed.

2.2.7.1 Cracking and Creaming Index

Cracking and the creaming index were studied according to the method reported by Ragavendra et al. [41], with modifications. The emulsions were separated in portions of approximately 10 g, and packed in glass tubes, at each time period the phase separation was evaluated. Cracking is a qualitative assessment. When complete phase separation of the emulsion

occurs, it is regarded as positive cracking. For formulations where there was partial separation, the upper part (creaming) was collected and weighed. The initial mass of each emulsion and the mass of the supernatant were used to calculate the extent of creaming, according to Eq. (2):

$$\%\ of\ Creaming\ = \frac{m_c}{m_T} \times 100 \quad (2)$$

Where: m_c is the mass of the supernatant and m_T is the total mass of emulsion.

2.2.7.2 Accelerated Thermal Stability

Accelerated thermal stability analyses of emulsions were performed after the thermocycling method [40]. The emulsions were submitted to five cycles with changes in incubation temperatures at 10°C and 30°C for a period of 12 hours for each temperature. The creaming and cracking rates were obtained at the end of each cycle as described in Item 2.2.7.1. In addition, the sum at the end of the five cycles was obtained as total creaming. Emulsions were considered stable when no separation was visually observed.

2.3 Statistical Analysis

The data obtained in this study were submitted to analysis of variance (ANOVA) and regression test using the SAS software, Studio version. The adequacy of the models was evaluated using the coefficient of determination (R^2), level of significance of the parameters of the model and analysis of the residue ($p<0.05$).

3 Results and Discussion

3.1 Physical-chemical Analysis

The results for pH and electrical conductivity of the six emulsion formulations showed no variations. The emulsions presented pH 5.94 ± 0.07 and undetectable conductivity, indicating the formation of water-in-oil (W/O) emulsion.

3.2 FT-IR Analysis

The FT-IR spectra of the main components used in the preparation of emulsions as well as the different formulations can be seen in Figure 1 (a and b). In the spectrum of the gelatine solution (GEL) seven characteristic bands were identified. The band (1) observed in the range 3700 - 2590 cm^{-1} is associated with the elongation of the –OH vibrations referring to the presence of water in the solution; its intensity, represented by the width of the band, indicates the numerous hydrogen bonds in the gel [42, 43]. Bands 3 (1641 cm^{-1}), 4 (1550 cm^{-1}) and 6 (1243 cm^{-1}), respectively, Amide I, Amide II and Amide III, reflect the C=O, C–N and N–H vibrations present in the collagen protein structure [42, 43]. Besides bands 2 (≈ 2100 cm^{-1}), 5 (1460 cm^{-1}) and 7 (range 1150 - 1030 cm^{-1}), characteristic of the free amino acid $–NH^{3+}$ vibrations [43] and carbohydrate C–H, C–O and C–O–C [44], both present as residues of the gelatin manufacturing process.

The fat spectra are represented by the red (BO) and black (CB) lines in Fig. 1a. They have the same vibrational modes, but those indicated by the arrows have different intensities. Bands 8 (2925 cm^{-1}), 9 (2855 cm^{-1}) and 14 (720 cm^{-1}) are related to the different vibrations of $–CH_2$ group and present higher intensity for CB. These bands are typical of stearic acid, majority fatty acid in cocoa butter and are also present in higher amounts in higher carbon chain fatty acids [42]. On the other hand, bands 10 (1745 cm^{-1}), 12 (1152 cm^{-1}) and 13 (1103 cm^{-1}) refer to the O–C=O, C–O and C=C–C–O vibrations of the triglyceride esters head [42, 45] and are more intense for babassu oil. In addition to these bands, the 1383 cm^{-1} (11) peak is linked to harmonic CH_3 vibrations in the tails of triacylglycerides [46].

All emulsions presented a combination of the vibrational modes of gelatine and fats, varying in intensity according to the continuous phase composition, as can be seen in their FT-IR spectra in Fig. 1b. The amounts of gelatine and lecithin solution in all emulsion formulations are fixed, with only the proportions in the BO and CB mixture varying. Thus, the differences highlighted by the rectangles are the result of molecular interactions between the fats and the aqueous phase and the structure of the emulsions.

In cocoa butter most of the fatty acids (≈90%) present have a higher carbon chain (between 16 and 20 carbons) [47] and are therefore more hydrophobic, that is, they tend to interact more strongly with each other and not with the gel. On the other hand, babassu oil has a large number of short or medium chain fatty acids (≈62,81%) [24], besides mono and diglycerides (≈0,51%) which are more hydrophilic substances than those of CB, which makes the intermolecular interactions of BO and interface and gel stronger. These differences are reflected in the different areas under the spectrum (3700 - 2590 cm^{-1}) highlighted by the solid black outline (Fig. 1a). The area under the curve decreases with the increase in the amount of BO in the emulsions, which is associated with the increase in the interaction forces between the oil

and the gel which decreases the amount of free water to vibrate. In addition, more water is exposed and available for interactions with the interface, formed by the gelatin and lectin of the emulsifiers, which is evident in the reduction of the intensity of the bands associated with the molecular vibration of the water.

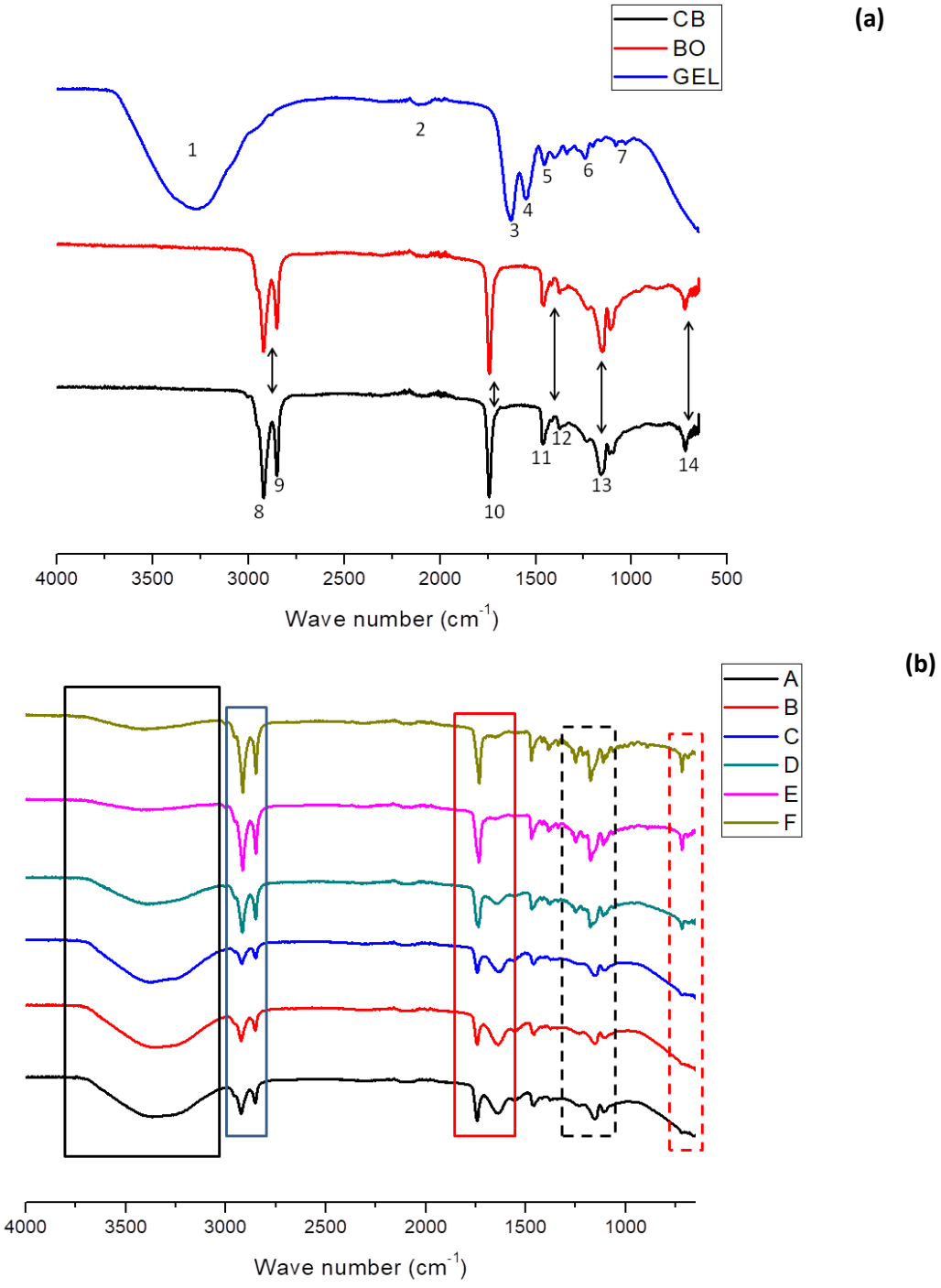

Figure 1. FT-IR spectra of the main emulsion ingredients (CB, BO and Gelatine) (a), FT-IR spectra of emulsions prepared with different quantities of CB and BO in the continuous phase (A - F) (b).

Similar reasoning can be considered for the assessment of the other highlighted areas. The peaks marked by solid blue and red and black and red dotted contours are linked mainly to the interactions between the carbon chains of fatty acids. A stable interface decreases the interaction of fat with the aqueous phase, so as the amount of BO in emulsions increases the intensity in the fat-related bands.

Furthermore, with the increase in the quantities of babassu oil, as the interfacial area increases, more gelatin is also present in this region, which consequently increases the gelatin-gelatin, gelatin-lectin, gelatin-water interactions, contributing to the reduction in the intensity of the bands (1641 cm^{-1} and 1550 cm^{-1}), associated with this gelling agent and emulsifier, highlighted in the solid red outline.

3.3 DRX Analysis

The DRX profiles of vegetable fats, BO and CB, and emulsions under study can be seen in Figure 2. The peaks represent ordering the medium and long distance indicating an organization of the crystalline lattice of the material. The halos show that the material has some organization, but little defined, characteristic of amorphous structure. In the case of oils and fats, diffraction is used to define polymorphism, which is the capacity of a chemical compound to form different crystalline structures [48], and is determined by the different subcells that their molecules can form, and forms of α, β′ and β are the typical polymorphic forms of fats [49].

Regarding cocoa butter, its polymorphic form is already well described in the literature [50]. It exists in the three different polymorphic forms mentioned above, the most dense and stable form being β, as shown in Figure 2a, the highest peak (d = 4.6Å) and other peaks (d = 5.42; 3.94 and 3.74Å) for the polymorph β and d = 4.15Å for the polymorphs α and β' [48].

On the other hand, the structure of babassu oil has not yet been described. Figure 2a shows that the BO has an amorphous structure, with identification of small peaks in the spacing 4.17Å and 4.20Å, corresponding to the polymorphic forms α and β', respectively. Additionally, it is not possible to know the extent of crystallinity, as the amorphous halo overlaps the peaks.

The formation of each polymorph is related to the structure of the triacylglycerol network, which in turn is influenced by the size of its fatty acids, the symmetry between them and the conformation of the glycerol group [48, 51, 52]. The BO is mainly composed of medium-chain fatty acids (≈57%) and has a certain amount of assymmetric triacylglycerols. These TAGs containing different types of fatty acids are more stable in β′ form [53]. CB has long chain fatty acids and more symmetric triacylglycerols, which makes it easier to fit in between the chains and the lower shortening, characteristic of the polymorph β.

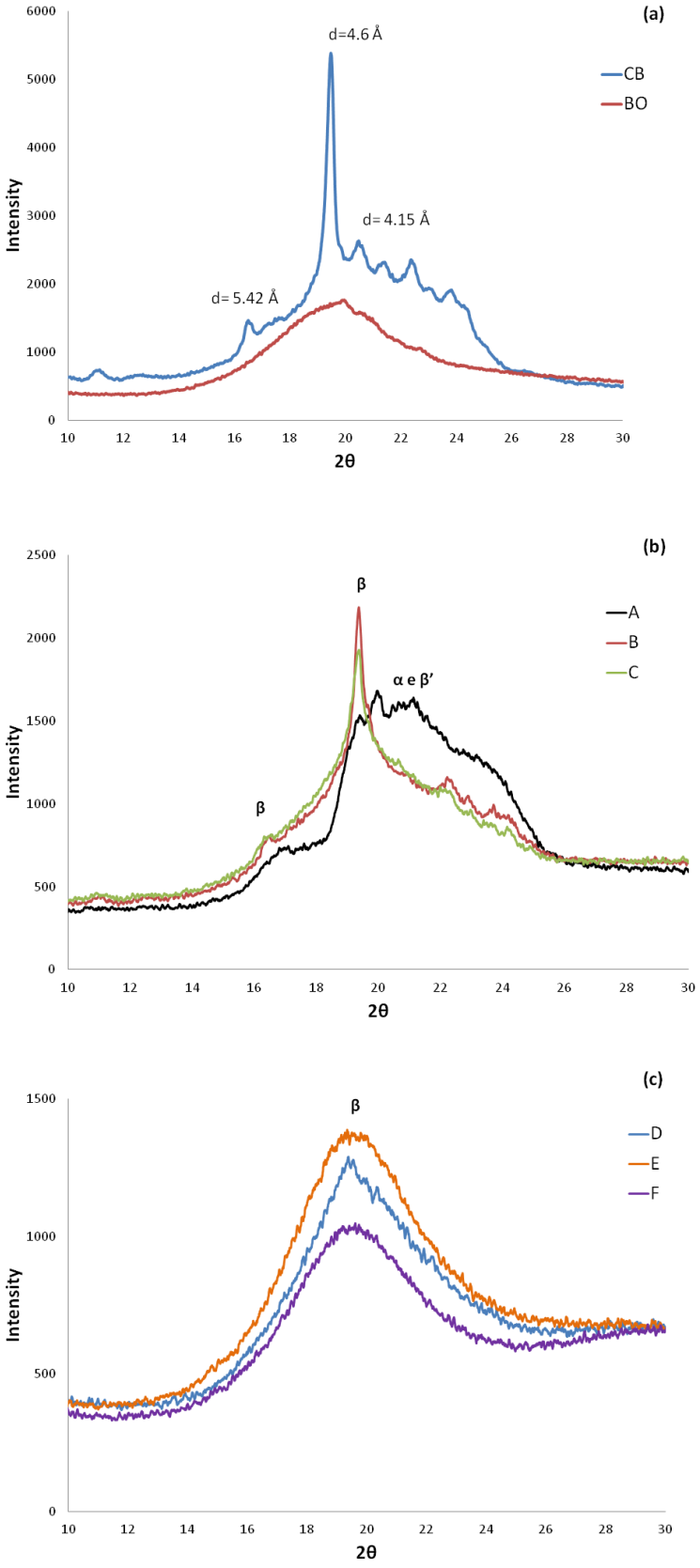

Figure 2. DRX profile of cocoa butter and babassu oil (a), emulsions containing the highest amounts of CB (b) and emulsions containing the highest amounts of BO (c).

The polymorphic forms identified in the emulsions, together with the distance d, are described in Table S1 in the Supplementary Material. The emulsions A, B and C, containing respectively 77.6; 62.08 and 46.56% cocoa butter presented the structure β, represented by the maximum peak at 19.37° 2θ, as the predominant polymorphism, but with less intensity than in pure butter. In Figure 2b it is possible to see that this crystallinity is greater for formulations B and C, where there are certain amounts of BO. Substances such as short and medium chain fatty acids, mono and diglycerides, as well as other minor substances, present in the BO, can interact more easily with the interface and the gel, allowing the molecules of CB to be free to organize themselves and form the fatty network, which is not the case in formulation A, where due to the size of the drops, the nature of CB's fatty acids and the low interaction of these molecules with the gel, the presence of the heterogeneous substance makes packaging difficult, suggesting that the number of fatty acids present in the form β has decreased and may have been transformed into other polymorphic states.

DRX patterns of D, E and F emulsions suggest predominantly amorphous nature. Nevertheless, it is possible to identify the presence of the polymorph β, represented by the maximum point at 19.37° 2θ. The amorphous nature of these emulsions depends on the relationship between CB and BO present. The DRX profile (Figure 2c) indicates that there is a specific proportion, between D and E, where amorphous behavior changes, and can be attributed to the balance between BO and gel interactions, both in the stabilization of fat-water interfaces and in the formation of the fat network, as previously discussed.

Finally, the presence of the state β, also in the F formulation, points out that the nature of the substances present in the BO (free fatty acids, mono and diglycerols) favors crystallization [54, 55]. Just like triglycerides, mono and diglycerides are polymorphic. Polymorphs such as α and β can be found for saturated mono- and diglycerides with a chain length shorter than 18 carbon atoms [56], case of those present in BO.

3.4 Thermal Analysis

The data acquired in the TG analysis of the material samples, BO, CB and gelatin solution and the emulsion, are represented in the curves of Figure 3.

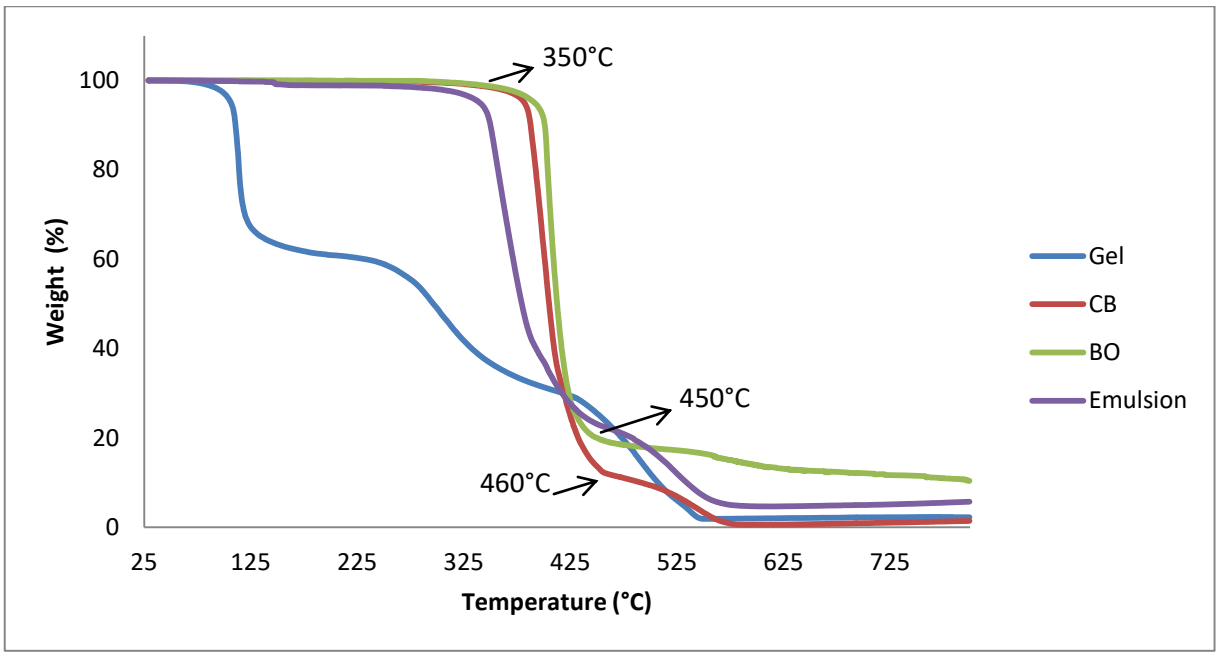

Figure 3. TG curves of materials and emulsion. CB - cocoa butter; BO - babassu oil; Gel - gelatin solution; Emulsion (Formulation C).

These curves represent the thermal behavior of the samples, where the thermal stability is represented by the temperature range in which the mass remains constant. The least stability is that of the gelatin solution (blue curve), where the marked loss of mass starts at around 50°C. In this case, the loss of mass is approximately 36.74% and occurs in the range between ≈ 50°C and ≈ 150°C and reflects the evaporation of free water, followed by two more steps. The second, represented by an additional mass loss of more than 30.7%, in the range ≈ 170°C to ≈ 400°C, where the release of water trapped in the gel occurs, and the third, between ≈ 400°C up to 540°C where the decomposition of the polymeric structure occurs, through hydrolysis, oxidation and pyrolysis reactions of gelatin collagen [57, 58].

The fat decomposition process (BO and CB) occurred in two stages, the first representing a marked degradation range, around 80% of the BO mass and 88% of the CB mass, between 350 - 450°C and 350 - 460°C, respectively. The second stage, occurs from the end of the first to approximately 560 ° C for both oils and is related to the combustion and carbonization of the material, the differences being attributed mainly to the fatty acid composition which is different for each of the oils, as previously discussed.

As expected, the emulsion decomposition (lilac curve) follows more closely the behavior of the oils, since they are the ones that form the continuous phase and are determinants in the thermal behavior in this case. In the temperature range between 100°C and 290°C, there is little loss of mass (≈ 2%) due to the evaporation of water and other volatile compounds, such as free fatty acids and monoglycerols present in fats. In the range from 290°C to 430°C there is a

marked loss, around 74% of the mass of the emulsion, which is related to the decomposition of fatty acids present in the continuous phase and also the release of water trapped in the gel phase. This step is advanced when compared to pure fats, which can be attributed to the lower interaction force between the fatty acid molecules and also to the instability and hydrolysis and oxidation reactions resulting from the presence of water in the mixture. Finally, the final phase, which goes up to ≈ 560°C related to the combustion and carbonization of the material. The remaining mass at 800°C was approximately 4.69% of the original mass, mostly formed by carbon and mineral residues.

The thermograms for the fusion behavior of each material and the emulsion are illustrated in Figure 4. The DSC heating curves showed only one endothermic curve for each of the materials, CB, BO, gelatine solution and also for the emulsion in the temperature range of 20 to 65°C. Gelatine solution and pure cocoa butter peaked at 37.85°C and babassu oil at 25°C, these temperatures correspond to the polymorphs β and α and β', respectively [34], and agree with the results obtained for the DRX standards of the samples, as discussed earlier.

The incorporation of the gelatine solution showed a decrease in the temperature of the endothermic peak. The introduction of the dispersed phase made it difficult to crystallize fats, and the peak emulsions were at 28.45°C, which is intermediate to the peak of pure fats. This shows the decrease in the formation intensity of the most stable polymorph (β), which has a structure with stronger bonds and, once these bonds are broken, the new structures formed have weaker interactions, generating a positive enthalpy variation, i.e. a decrease in the endothermic peak. These results are in agreement with the results obtained for the transition enthalpies of the emulsions that show a tendency to decrease as the structure becomes more amorphous, -92.83 J/g (Emulsion A), -66.89 J/g (Emulsion B), -54.14 J/g (Emulsion C), -31.85 J/g (Emulsion D) and not determined for emulsions E and F.

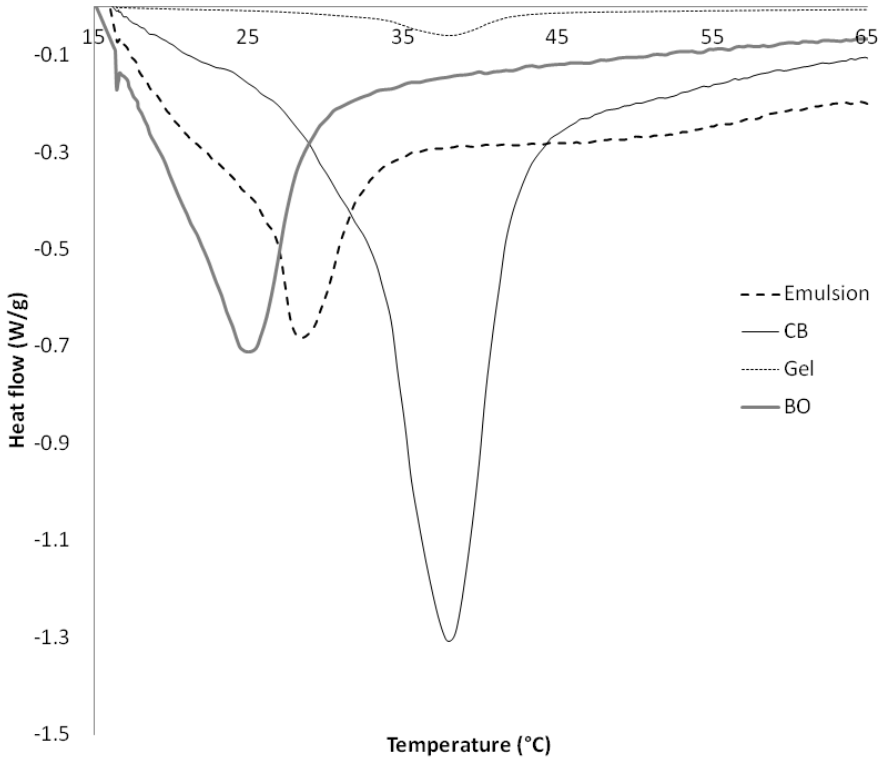

Figure 4. Thermograms of the fusion of materials and emulsion. CB - cocoa butter; BO - babassu oil; Gel - gelatin solution; Emulsion (Formulation C).

The fusion enthalpies of the emulsions were calculated by the integral of the endothermic peak areas of each formulation. As the amount of BO increases and the amount of CB decreases in the fat phase, the enthalpies decrease. As previously discussed, this is the result of the decrease in the interaction forces between molecules in each formulation, where the structure becomes more unstable and the necessary energy decreases to break the interactions and pass from the solid to the liquid state, which is a reflection of the greater heterogeneity in the organization of molecules and fatty acids with different chain lengths, saturated and unsaturated, increasing the softness of emulsions [53].

3.5 Mechanical Analysis

3.5.1 Emulsion Hardness

During preliminary tests and also in the execution of the experiments, the six emulsions formulated in this study presented fragile materials. The predominant failure pattern was a longitudinal fracture with the subsequent formation of smaller pieces, as illustrated in Figure S1 in the Supplementary Material.

Food hardness is related to the idea of material firmness, and a sensory property is defined as the force required to compress food between the tongue and the palate or between the molar teeth, and instrumentally, as the force required to cause a certain deformation. The stress supported by a material is proportional to the force required to break down the interaction forces between its molecules. In the case of W/O emulsions, the force will be greater according to the higher the organization of the lipids and the lower the structural defects in the crystals in the fat network (continuous phase), as demonstrated by Sullo et al. [59], in a study on different formulations of cocoa butter emulsions. Similar behavior was observed in this study (Figure 5), where, as the proportion of BO increases in emulsion formulations, the maximum force supported by the material before fracture decreases. This is related to the increased gel dispersion in the emulsion, which makes the structure more heterogeneous and viscous, and is also in line with previous results for FT-IR, DRX and DSC analyses, which showed a decrease in the forces of the constituent interactions as the amount of BO in the continuous phase was increased, resulting in a lower amount of energy needed to break the material.

CB has long chain fatty acids, mainly grouped in symmetric triacylglycerols [50], which ensures better packaging and a more organized and denser molecular arrangement, characteristic of the crystalline form β, more stable and predominant in this fat. In addition, because it has longer molecular chains, CB is able to organize itself by forming a kind of protective shell around the dispersed phase droplets [60], which at temperatures lower than its melting temperature (e.g., refrigeration) solidify and stiffen the emulsion.

On the other hand, the BO is formed mainly by medium chain fatty acids and has a certain amount of asymmetric triacylglycerols, decreasing its packaging capacity and therefore presents certain softness. Thus, as the amount of BO in the emulsion increases, the packaging and approximation of the lipid molecules diminish and the intermolecular forces between the different fatty acids become weaker, decreasing the hardness of the material [60], as already demonstrated in the results presented in the XRD analyzes. In addition, this structural weakening that occurs as the amount of BO in the continuous phase increases can be explained by the presence of interfacially active species at the aqueous/fat droplet interfaces that can affect the nucleation and growth of the continuous fatty phase crystals [51], which decreases the stable solid junctions and reduces the overall strength of the material.

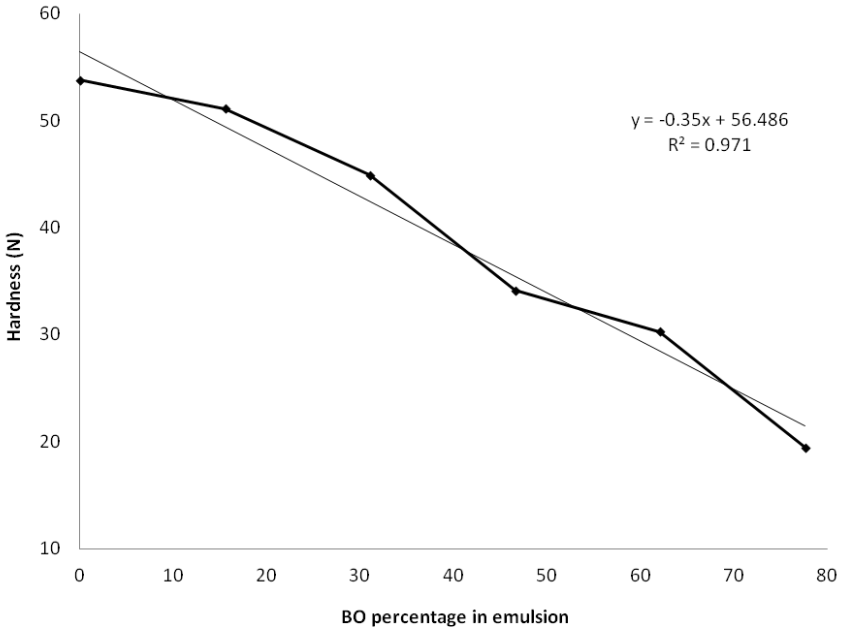

Figure 5. Hardness behavior of the emulsions with the increased level of substitution of cocoa butter by babassu oil in the continuous phase.

3.5.2 Spreadability

As expected, the results for the spreadability extension for the different emulsion formulations indicated that the spreadability depends on the applied load and that increasing this load increases the spreadability. The study temperature for spreadability (20°C) was chosen because it is the temperature at which butter and margarine type products should be stable and semi-solid [61].

The data show that, as the amount of BO increases, the rate of spreadability also increases and not proportionally (non-parallel curves in Figure S2, in the Supplementary Material). The largest slopes are in the E and F curves that represent the emulsions with the highest amounts of BO (62.08 and 77.6%, respectively) and that agree with the results observed for the mechanical hardness property. At 20°C, the BO is partially melted and the solid part of its fat is organized in the forms α and β', which gives the softness and consequent higher spreading rate, between ≈6% and ≈104%, for loads of 25g and 200g, respectively. On the other hand, at this temperature, CB is almost totally solid, the dispersed gel is trapped inside the lipid net, and the spreading rate of formulations A - D is small, between null and ≈ 26%, for loads of 25g and 200g, in this order.

3.6 Stability

3.6.1 Accelerated Thermal Stability

During the thermocycling tests none of the emulsions studied was cracked, that is, there was no complete separation of its main components, continuous and dispersed phase. The A and B emulsions, containing the smallest amounts of BO and the largest amounts of CB remained stable during the five thermal cycles. Formulations C through F were destabilized soon after the first thermal cycling, and the extent of creaming was dependent on the different concentrations of BO and CB in the greasy phase. For formulations C and F, the creaming formation is more significant between cycles 1 and 2, while for formulations D and E, the creaming rate increases uniformly over all cycles, as can be seen in Figure 6a.

Regarding the composition of the fatty phase of emulsions, the increase in the substitution of CB by BO increases the separation of this phase, but only to a certain extent. When the amounts of CB and BO reach 15.28% and 62.32% of the emulsion, there is a decrease in creaming, as can be seen in Figure 6b.

The different thermal stabilizations of the emulsions studied are essentially related to two factors: (1) the strength of the lipid network formed by the continuous phase, which influences the melting point of cocoa fats (≈ 37°C) and babassu (≈ 25°C) and their mixtures; (2) the fatty acid composition and minority components of each of these fats, which is related both to the rigidity of the continuous phase and to the stabilization of the droplets of the dispersed phase [54].

Factor 1 seems to govern the stability processes of A and B and also the destabilization of C, D and E. With respect to formulations A and B, they remain stable, probably due to the physical impediment to the release of the gel and/or BO present in these emulsions. In these cases, as the fatty phase is mostly formed by CB (which has higher crystallization and melting points) during the period of incubation of the emulsions, it is the fatty acids of this fat that induce the organization of the lipid network, more packaged and crystalline and with higher fusion temperature. Thus, as the maximum temperature in thermocycling is 30°C, the lipid net formed by CB remains solid, forming a physical barrier that prevents the passage of the gel and/or BO and the consequent formation of creaming.

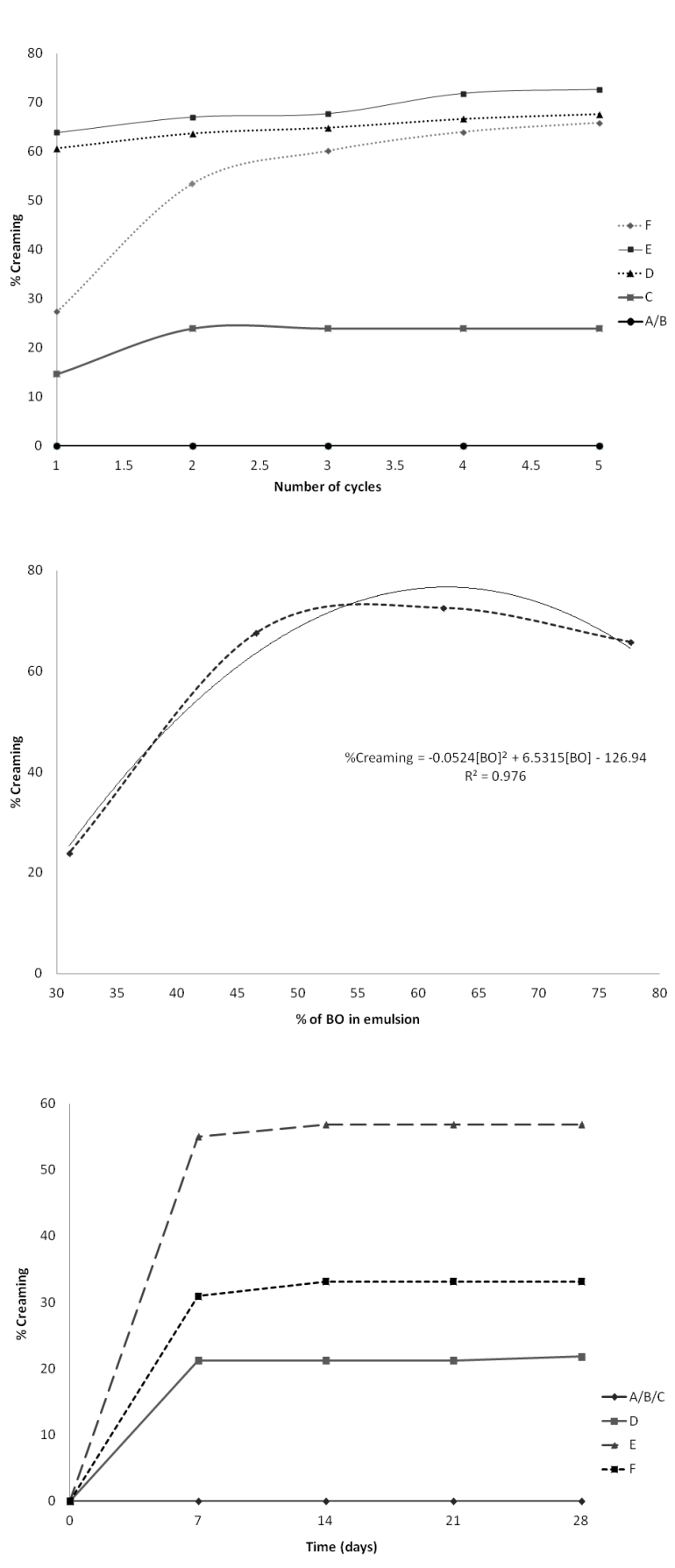

Figure 6. Creaming formation after 5 cycles of thermocycling (10°C/12h - 30°C/12h), of the different emulsions containing BO, CB and gelatine solution (A, B, C, D, E, F) (a) and as a

function of BO concentration (b). Creaming formation of the different emulsions (A, B, C, D, E, F) after 28 days of storage at room temperature (25 ± 2°C) (c).

A similar mechanism occurs with the C emulsion, which has 46.56% of CB and 31.04% of BO. For this formulation the maximum creaming is in the second cycle (Figure 6a) and is around 24%, with no additional formation in cycles 3 to 5. During the temperature oscillations in the first cycles, most of the BO fuses, because it has a less organized structure, with melting temperature lower than 30°C, and is detached from the lipid matrix of the continuous phase (supernatant), the rest remains in the matrix, either because they are interacting with the crystals of CB, or because they are stabilizing the gel/oil interfaces, since the BO has fatty acids with smaller carbon chains, free fatty acids, mono and diacylglycerols, among other minority substances, which have high surface activity and are able to interact more strongly with the protein molecules of the gel networks.

With regard to D and E emulsions, right after the first thermocycling there is a large formation of creaming (between 60-64%) and in the following cycles the destabilization of emulsions is small and constant. During the incubation period, fat solidification occurs in a less organized way, due to the steric impediment between the different structures of the molecules of CB and BO fatty acids and triacylglycerols, which does not allow the approximation of these molecules and the necessary packaging for the formation of a crystalline structure. This low organization reduces the fusion point of fat (CB and BO) that during the hot stage of the cycle liquefies and detaches from the emulsion, and the small amount of lipids that remains in the mixture are those closest to the gel/fat interface.

For F emulsion, where the greasy phase is composed of BO only, a combination of factors 1 and 2 is linked to the creaming formation process and its extension, respectively. Due to the nature of their fatty acids, as previously discussed, the molecules are not able to approach each other and the crystalline structure formed is composed of crystals β', which has a lower melting point [68]. In addition, the dispersion of the gel, between this fat, further decreases the structural organization of the emulsion, because some components present in the BO can interact more strongly with the gel than those present in the CB, which causes the formation of weaker zones in the matrix and the amorphous characteristic of the material, which is in accordance with the highest percentage rate of creaming formation until the second cycle. On the other hand, free fatty acids, mono and diacylglycerols, present in the BO, are molecules that can act as surfactants, positioning themselves in the layers between the dispersed phase (gel) and continuous phase (fat) to stabilize the emulsion, decreasing the extent of creaming and its formation rate over cycles 3 to 5. These active molecules make the link between the gel and the

oil layers that remain stable in the emulsion, which also agrees with the increased stability in emulsions with concentrations greater than 62.32% of BO.

3.6.2 Stability after Storage

During the 28-day storage period none of the emulsions were cracked. In cases of refrigerated storage and at 20°C, all formulations remained visually stable. During storage at room temperature (25 ± 2°C), formulations A, B and C remained stable for 28 days, while formulations D, E and F showed maximum creaming formation until the seventh day, with no further phase separation, as can be seen in Figure 6c.

According to the regression analysis carried out for the formation of creaming in storage: % Creaming = - 0.1217[BO]^2 + 15.481[BO] - 435.05 (R^2=0.998), phase separation will be maximum when the amount of BO reaches 63.6% of the emulsion, decreasing in values above this concentration, which is in agreement with the accelerated thermal stability test discussed above and which explains the changes occurred for this behavior.

4. Conclusion

The results obtained in this research demonstrated that it is possible to produce stable A / O emulsions from mixtures of babassu oil and cocoa butter and gelatin solution. The stability and hardness of the emulsions is greater with the decrease in the proportion of babassu oil in the formulation, being completely stable, for a period of 30 days, emulsions containing ≈38% (w / w) or less of BO. When refrigerated storage, all formulations remained stable throughout the storage period. Thus, as the results show, emulsions have different characteristics and all show potential for application in the industry, either as ingredients in different food products, such as chocolates, bakery products, ice cream, for example, or as lipid bases in cosmetic products, such as lotions and makeups.

5. Acknowledgment

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Conflict of Interest

Not one.

6. References

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Supplementary Material

Table S1. Polymorphic forms identified in emulsions containing different proportions of CB and BO.

Emulsion	Short Spacing (Å)	Polymorphic form
	4.57	B
A	4.5	B
	4.2	α, β’
	4.58	B
B	3.9	B
	3.75	α, β’
	5.4	B
C	4.58	B
	4.2	α, β’
D	4.58	B
E	4.58	B
F	4.58	B

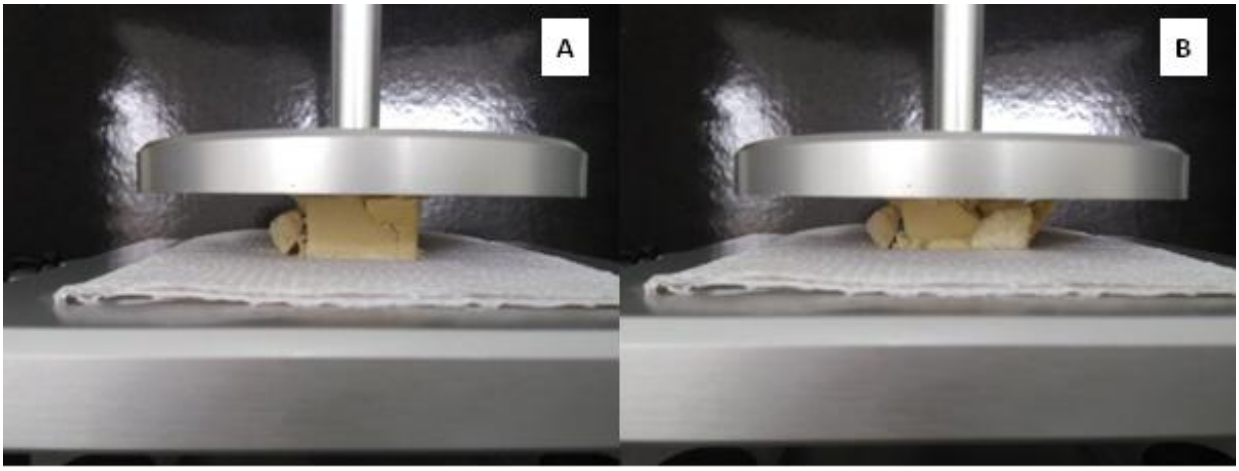

Figure S1. Predominant pattern of fracture propagation in emulsions with different CB and BO ratios in the continuous phase. (A) Initial longitudinal fracture; (B) Formation of smaller pieces

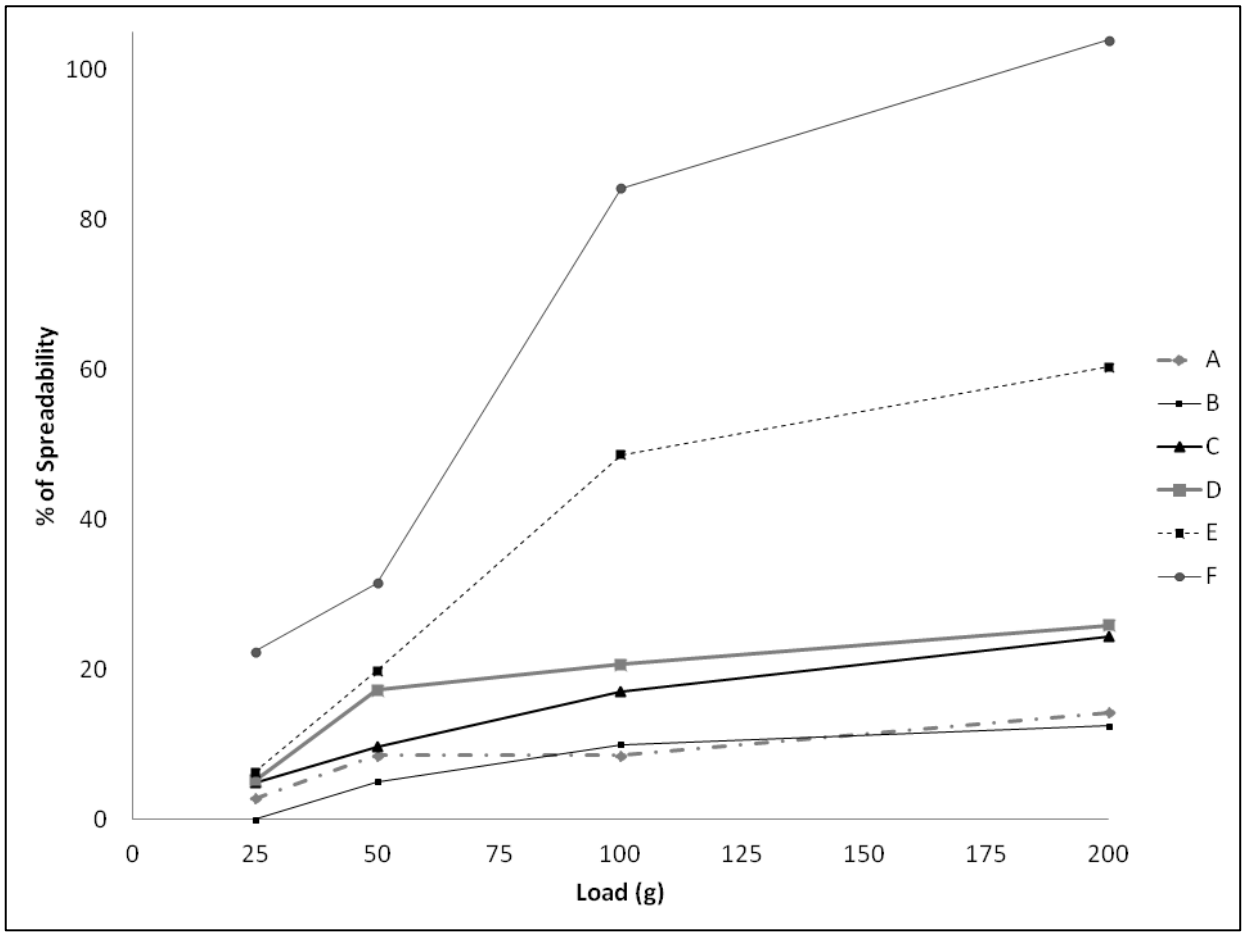

Figure S2. Spreadability of different emulsions w/o with increasing levels of replacement of CB by BO in the continuous phase (A - F)

Capítulo 6

Considerações Finais e Perspectivas Futuras

1 CONSIDERAÇÕES FINAIS

O óleo de babaçu é um óleo comestível, sendo extraído comumente de forma artesanal, por dois métodos principais, através do cozimento das amêndoas, onde obtém-se o óleo virgem de babaçu, e por prensagem mecânica das amêndoas do coco, obtendo-se o óleo extra-virgem de babaçu.

Os resultados demonstraram que o processo de extração modifica as características químicas e físicas dos óleos, porém, tanto o óleo virgem de babaçu quanto o extra-virgem estão em conformidade com os requisitos determinados pelos órgãos reguladores, tanto brasileiro, como também Americano e Europeu. Dentre as diferenças encontradas, destaca-se a cor e os índices de acidez e peróxidos, onde o óleo virgem é mais escuro e apresenta valores mais elevados, respectivamente. E ainda o perfil lipídico, onde o método de extração interfere nas quantidades dos ácidos graxos presentes em cada óleo, contudo sem interferir nos ácidos graxos encontrados, onde destaca-se os saturados, principalmente láurico e mirístico.

Além disso, o método de extração também resultou em diferentes atividades antioxidantes para os dois tipos de óleos de babaçu estudados. A extração com uso de calor foi capaz de incorporar uma quantidade maior de compostos bioativos, resultando numa maior capacidade antioxidante para o óleo virgem de babaçu.

Com relação as características térmicas, ambos óleos, apresentaram alta estabilidade térmica. Seus pontos de cristalização e fusão, em torno de 13°C e 25°C, respectivamente, são semelhantes ao óleo de palmiste, e permitem sua aplicação direta na formulação de diferentes produtos, como chocolates, sorvetes, margarinas, cremes e recheios para panificação, propiciando diferentes características e texturas a depender do modo de processamento e/ou armazenamento dos produtos alimentícios.

Além disso, foi possível produzir emulsões A / O estáveis a partir de misturas de óleo de babaçu com manteiga de cacau e solução de gelatina, sendo que a maciez das emulsões foi maior com o aumento da proporção de óleo de babaçu na formulação. Devido às características químicas e físicas das diferentes gorduras, óleo de babaçu e manteiga de cacau, era esperado que as emulsões apresentassem características distintas, contudo, todas apresentam potencial de aplicação na indústria de alimentos e/ou cosmética.

Cada formulação pode ser utilizada com funcionalidades diferentes em diferentes produtos alimentícios, como chocolates ou outros produtos com sabor chocolate (caso das emulsões com maior teor de manteiga de cacau), e as emulsões mais macias, como substitutas de manteiga de leite ou margarinas ou outros cremes vegetais em massas, biscoitos, bolos e pães, por exemplo. Além de também serem opções de bases lipídicas para produtos cosméticos.

2 PERSPECTIVAS FUTURAS

O processo de caracterização e aplicação do óleo de babaçu proposto nesta tese foi apenas o início do caminho para maior aplicação industrial desta matéria-prima brasileira. Existem ainda algumas etapas a serem alcançadas antes da expansão do uso deste óleo na indústria de alimentos.

Em relação à produção do óleo, é necessário investir em pesquisas que permitam o controle do processo de obtenção e que garantam a qualidade e maior padronização do óleo processado, uma vez que é imprescindível para a indústria ter um mínimo controle em relação as características da sua matéria-prima.

Em relação aos estudos fundamentais, é necessário compreender as interações deste óleo com outros ingredientes presentes comumente na formulação dos alimentos processados, como proteínas, carboidratos e diferentes aditivos, como corantes, conservantes, estabilizantes, edulcorantes, entre outros.

Como perspectiva imediata, é importante a aplicação das emulsões propostas neste estudo em novos produtos ou como alternativa em produtos já existentes e sua avaliação quanto às características físico-químicas, de estabilidade, sensoriais e de aceitação diante dos consumidores, como por exemplo, o desenvolvimento de um creme de cacau, castanhas e óleo de babaçu (emulsão) genuínamente brasileiro, a “Babaçutela”.