UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ENGENHARIA DE ALIMENTOS

LARRY OSCAR CHAÑI PAUCAR

ESTUDO DA EXTRAÇÃO SUPERCRÍTICA COM E SEM ACOPLAMENTO DE PRENSAGEM MECÂNICA A FRIO DE MATÉRIAS-PRIMAS LIPÍDICAS

STUDY OF SUPERCRITICAL EXTRACTION WITH AND WITHOUT COLD MECHANICAL PRESSING COUPLING OF LIPIDIC RAW-MATERIALS

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Thesis presented to the Faculty of Food Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Ph.D in Food Engineering.

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RESUMO

O estudo avaliou a extração com fluido supercrítico (SFE) e SFE acoplado à prensagem mecânica a frio (PMF) de matérias-primas oleaginosas. Na primeira parte do estudo, o processo SFE foi avaliado para determinar o efeito da pressão e temperatura no rendimento de extração, cinética de extração e composição dos extratos, utilizando três matérias-primas: polpa de buriti (*Mauritia flexuosa*) (MF), sementes de sucupira (*Pterodon emarginatus*) (PE) e baru (*Dipteryx alata*) (DA). Na etapa seguinte, a semente de baru foi selecionada devido à sua disponibilidade como matéria-prima para avaliar a extração com fluido supercrítico assistida por prensagem (SFEAP), os resultados foram comparados com o SFE. Finalmente, um novo método de extração foi proposto para superar as desvantagens do SFEAP, especialmente aquelas resultantes do funcionamento sequencial do SFE e PMF. O novo método visa o funcionamento simultâneo do SFE e PMF. Os resultados da extração por SFE mostram que a pressão e temperatura tiveram efeito significativo no rendimento de extração para as três matérias-primas, onde 51,5 g óleo/100 g MF (40 MPa e 60 ºC), 40 g óleo/100 g PE (30 MPa e 40 ºC) e 21,9 g óleo/100 g DA (35 MPa e 45 ºC) são os maiores rendimentos para cada matéria-prima. Na extração do óleo de baru pela SFEAP, a melhor condição de extração foi semelhante à observada na SFE, obtendo um maior rendimento de 28,6 g óleo/100 g DA. A modelagem matemática da cinética de extração, utilizando o modelo Spline, mostrou que a prensagem no SFEAP aumenta a taxa de transferência de massa do período CER e FER, observada no SFE. Os extratos obtidos por SFE e SFEAP foram ricos em ácidos graxos insaturados e apresentaram bioativos da família dos terpenos. Os resultados da extração sCO_2+PMF obtidos a diferentes pressões de pistão (P_P) e Pressão de extração (P_E), sugerem que a melhor combinação foi de 15 MPa (P_P) e 10 MPa (P_E). Nesta condição o rendimento de extração foi de 25,1 g óleo/100 g DA. A principal vantagem do processo de extração simultânea foi a diminuição da pressão de extração de 35 MPa para 10 MPa. O processo sCO_2+PMF resulta promissória para a produção de extratos bioativos, mas se requer mais estudos para aplicação em outras matérias primas e o aumento de escala do processo.

Palavras-chave: equipamento de extração supercrítico; modelo spline; óleos comestíveis; SFE; SFEAP; sCO_2+PMF.

ABSTRACT

The study evaluated the supercritical fluid extraction (SFE) and SFE coupled to the mechanical cold pressing (MCP) of oleaginous raw-materials. In the study first part, the SFE process was evaluated to determine the effect of pressure and temperature on extraction yield, extraction kinetics, and extracts composition, using three raw-materials: buriti pulp (*Mauritia flexuosa*) (MF), Sucupira seeds (*Pterodon emarginatus*) (PE), and Baru (*Dipteryx alata*) (DA). In the following stage, the baru seed was selected due to its availability as a raw-material to evaluate the supercritical fluid extraction assisted by pressing (SFEAP), the results were compared with the SFE. Finally, a new extraction method has been proposed to overcome the disadvantages of SFEAP, especially those resulting from the sequential functioning of SFE and MCP. The new method aims at the simultaneous operation of the SFE and MCP. The results of the extraction by SFE show that the pressure and temperature had a significant effect on the extraction yield for the three raw-materials, where 51.5 g oil/100 g MF (40 MPa and 60 ºC), 40 g oil/100 g PE (30 MPa and 40 ºC), and 21.9 g oil/100 g DA (35 MPa and 45 ºC), are the highest yields for each raw-material. In the extraction of baru oil by SFEAP, the best extraction condition was similar to that observed in SFE, obtaining a yield of 28.6 g oil/100 g DA. The mathematical modeling of the extraction kinetics, using the Spline model, showed that pressing in the SFEAP increases the mass transfer rate of the CER and FER period observed in the SFE. The extracts obtained by SFE and SFEAP were rich in fatty acids unsaturated and showed bioactive from terpenes' family. The sCO_2+MCP extraction results obtained at different piston pressures (P_P) and extraction pressure (P_E), suggest that the best combination was 15 MPa (P_P) and 10 MPa (P_E). In this condition the extraction yield was 25.1 g oil/100 g DA. The main advantage of the simultaneous extraction process was the reduction of the extraction pressure from 35 MPa to 10 MPa. The sCO_2+MCP process is promising for the production of bioactive extracts, but it is necessary more studies for application in other raw materials and to increase the scale of the process.

Keywords: supercritical extraction equipment; spline model; edible oils; SFE; SFEAP; sCO_2+MCP.

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CAPÍTULO I: *Introdução Geral e Objetivos*

1.1. Introdução

A produção de bioativos se expandiu rapidamente nos últimos anos, técnicas como a destilação molecular (KETENOGLU, 2021), extração por ultrassom (OJHA *et al.*, 2020), líquidos pressurizados (GARCIA-MENDOZA *et al.*, 2017) e fluidos supercríticos (HERRERO *et al.*, 2015), são frequentemente reportados na literatura como técnicas de extração promissoras. A tecnologia supercrítica tem capturado um especial interesse dos cientistas e empresas industriais para a produção de fitoquímicos de alto valor biológico, devido a seletividade da extração, temperaturas baixas de operação, tempos mais curtos de extração com maior rendimento do que os métodos convencionais. O dióxido de carbono é o solvente mais amplamente utilizado no processo *supercritical fluid extraction* (SFE), na literatura são reportados a extração de bioativos de uma grande diversidade de matérias-primas (CATCHPOLE *et al.*, 2018; HERRERO *et al.*, 2015).

O uso de CO_2 supercrítico para a extração de fitoquimicos é a aplicação mais simples e amplamente estudada. Outras aplicações mais complexas são a cromatografia de fluidos supercríticos, nucleação, processamento de polímeros, reações químicas e enzimáticas (MCHUGH; KRUKONIS, 1994). A melhoria da eficiência e eficácia desta técnica foram exploradas empregando cossolventes (MELO *et al.*, 2020), pré-tratamentos das matérias-primas com enzimas (MUSHTAQ *et al.*, 2017) e modificando o equipamento de extração. As modificações do equipamento de extração estão em desenvolvimento, algumas patentes de modificação do equipamento supercrítico estão disponíveis no site Orbit (ORBIT, [*s. d.*]), como por exemplo, a implementação de um sistema multicamada com autoaperto no interior da coluna de extração (PENGFEI; XIAOJIE; YURONG, 2018a, 2018b) e a incorporação de um componente de filtro no interior da coluna de extração para aumentar a área de contato com o fluido (XIANG *et al.*, 2019). Outras inovações no processo de extração supercrítica incluem a incorporação da técnica de ultrassom (LIU; OU; GREGERSEN, 2020) e prensagem mecânica frio (JOHNER; HATAMI; MEIRELES, 2018). A diferença do ultrassom, a implementação da prensagem a frio no processo de extração supercrítica resulta interessante, pois a prensagem a frio é uma técnica de baixo custo de implementação e é uma tecnologia simples em termos de manutenção e operação.

A fusão da extração supercrítica e a prensagem a frio foi denominado *Supercritical Fluid Extraction Assisted by Pressing* (SFEAP). A aplicação deste novo método incrementou os rendimentos de extração de óleo volátil de botões de cravo (*Syzygium aromaticum*) (HATAMI *et al.*, 2019), extrato de sementes de *Foeniculum vulgare* (HATAMI; JOHNER; MEIRELES, 2018) e óleo de polpa de *Caryocar brasiliense*

(JOHNER; HATAMI; MEIRELES, 2018). O modelo *Spline* descreveu adequadamente a cinética de extração do óleo de *C. brasiliense* obtida por SFE e SFEAP, observando-se no SFEAP uma maior inclinação da reta que representa o período *constant extraction rate* (CER) e *falling extraction rate* (FER), isto indica provavelmente uma maior taxa de transferência de massa nesses dois períodos em comparação à extração supercrítica (JOHNER; HATAMI; MEIRELES, 2018).

O processo de extração por SFEAP é realizado em duas etapas. A primeira etapa consiste na prensagem mecânica a frio, nesta etapa é utilizado um dispositivo acoplado à coluna de extração. A segunda etapa é a própria extração supercrítica. O primeiro é feito manualmente e requer etapas adicionais ao processo de extração SFE, como a montagem e desmontagem do dispositivo de prensagem, isso é desvantajoso porque expõe o extrato ao oxigênio do ambiente, a matéria-prima adere às paredes do pistão da prensa resultando em perdas e um aumento no tempo total de extração. Portanto, resulta interessante desenvolver um processo de extração integrando o SFE e a prensagem mecânica a frio, ambos funcionando em linha.

O presente estudo foi desenvolvido utilizando três matérias-primas, polpa de buriti (*M. flexuosa*) (Figura 1.1), sementes sucupira (*P. emarginatus*) (Figura 1.2) e baru (*D. alata*) (Figura 1.3). As três matérias-primas não foram anteriormente utilizadas para estudar a extração supercrítica acoplada a prensagem mecânica a frio.

Figura 1.1. (A) Cacho de buriti, (B) frutos após tratamento térmico e (C) fruto cortado transversalmente.

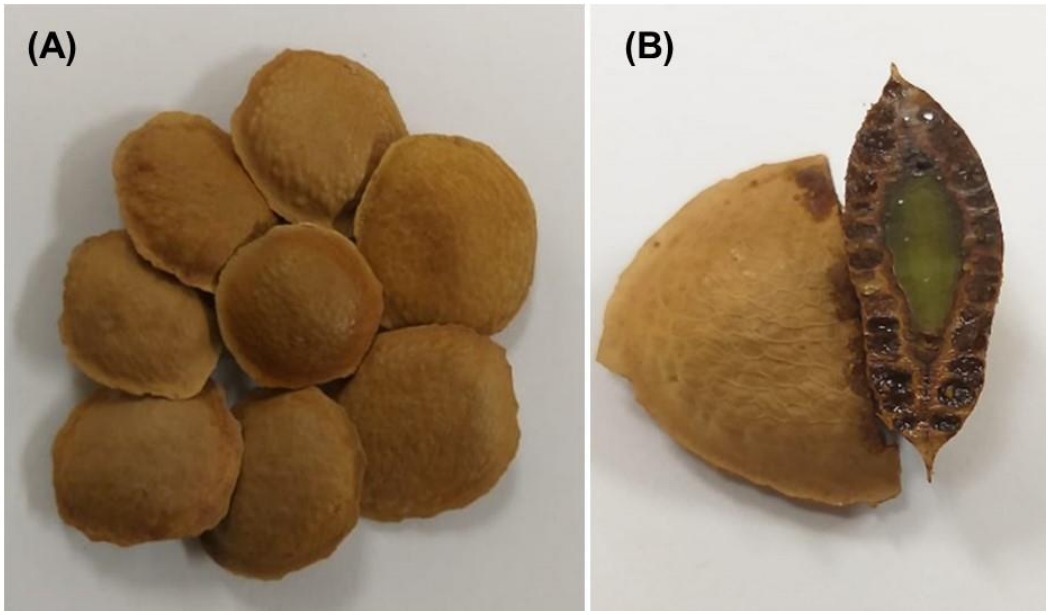

Figura 1.2. (A) Sementes de sucupira e (B) corte da semente.

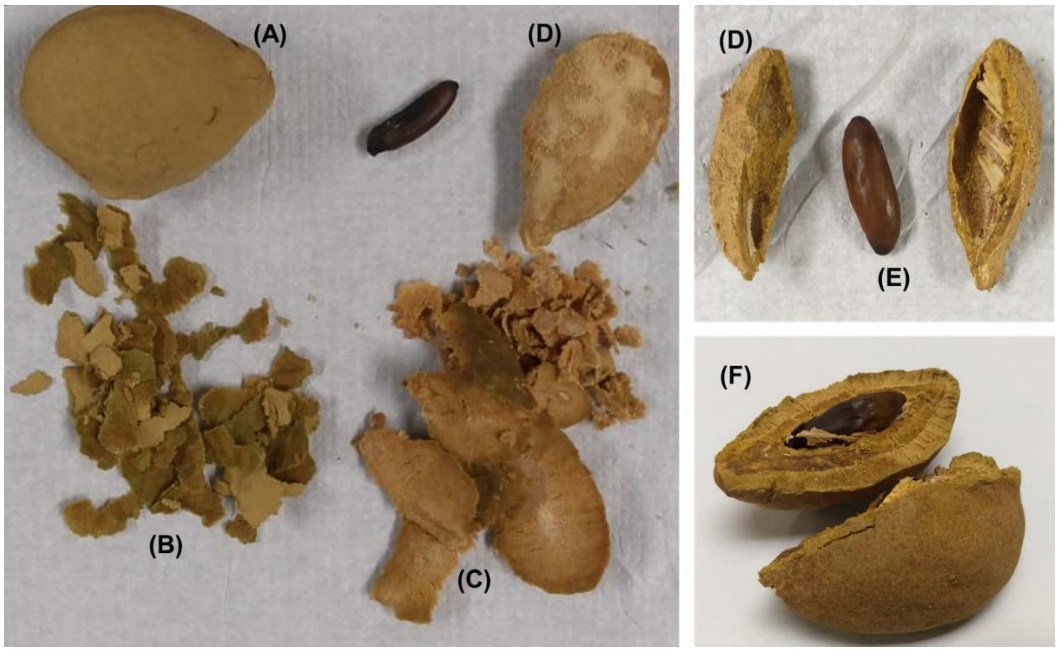

Figura 1.3. (A) Fruta baru inteira; (B) Casca (Epicarpo); (C) Polpa (Pericarpo); (D) Carcaça dura (Endocarpo); (E) Semente; (F) Corte longitudinal do fruto.

Os estudos da extração supercrítica das três matérias-primas são insuficientes. No caso do buriti, o mesocarpo + epicarpo foi utilizado para a extração supercrítica de carotenoides (FRANÇA *et al.*, 1999), nesse estudo foi avaliado duas pressões e uma

temperatura, se determinou o rendimento global, perfil de ácidos graxos e outros princípios ativos. Por outra parte, o extrato da semente de sucupira obtido por extração subcrítica com CO_2 (20°C e 12 MPa) mostrou potencial para o tratamento de *Leishmania amazonenses*, os autores do estudo atribuíram esse efeito à presença de compostos da família dos terpenos (SANTOS *et al.*, 2016a). A natureza apolar dos terpenos permite que sejam extraídos usando dióxido de carbono supercrítico (HATAMI; JOHNER; MEIRELES, 2017). As sementes de baru possuem uma alta qualidade nutricional (FERNANDES *et al.*, 2010; DE OLIVEIRA SOUSA *et al.*, 2011). Na medicina tradicional, o baru é usado para tratar uma ampla variedade de doenças (BENTO *et al.*, 2014; RIBEIRO *et al.*, 2017). A extração de óleo da semente de baru foi avaliada utilizando a extração supercrítica convencional (SFE) e assistida por ultrassom (SANTOS *et al.*, 2016b), observou-se que a melhor condição de extração por SFE foi a 35 MPa entre 40 a 50 °C, o rendimento foi entre 22,6 e 22,8 g/100g SB, respectivamente. A aplicação de ultrassom no SFE não teve efeito significativo no rendimento global da extração e na composição de ácidos graxos. De acordo com as considerações teóricas descritas nesta seção são formuladas os objetivos e a justificativa deste estudo.

1.2. Justificativa

O presente trabalho consiste na obtenção de extratos de matérias-primas oleaginosas aplicando extração supercrítica com e sem prensagem mecânica a frio. E propor um novo processo de extração combinado a extração supercrítica convencional com CO_2 e a prensagem mecânica a frio. A ideia do projeto vem das desvantagens observadas no método SFEAP quando comparado ao SFE. O novo processo de extração visa superar essas desvantagens e se manter superior ao SFE em termos de rendimento de extração. A validação do novo processo de extração com CO_2 supercrítico e a prensagem mecânica a frio será feito em um protótipo montado exclusivamente para este fim. Como foi relatado nos artigos mais recentes sobre o método SFEAP, ainda há a limitação do funcionamento sequencial do SFE e da prensagem, isso leva a um aumento no tempo de extração, exposição da matéria-prima e do extrato ao meio ambiente durante a extração, possíveis perdas de matéria-prima e extrato na desmontagem do dispositivo de prensagem, aumento dos custos operacionais e possível perda da qualidade dos extratos bioativos. Portanto, o presente estudo visa propor um processo de extração simultaneamente com dióxido de carbono supercrítico e prensagem mecânica a frio (sCO_2+PMF) com o intuito de melhorar

as desvantagens do SFEAP e se apresentar como um processo alternativo com maior eficiência para a recuperação de princípios ativos, especialmente para matérias-primas com alto conteúdo de extratos oleosos.

1.3. Objetivos

1.3.1. Objetivo geral

Avaliação da extração supercrítica e da extração supercrítica acoplada a prensagem mecânica a frio de matérias-primas oleaginosas, visando a obtenção de extratos bioativos de forma mais eficiente.

1.3.2. Objetivos específicos

- Avaliar o processo SFE da polpa de buriti (*M. flexuosa*), sementes de sucupira (*P. emarginatus*) e baru (*D. alata*), a diferentes condições de extração para determinar o efeito no rendimento global, cinéticas de extração e composição.
- Avaliar diferentes condições de extração aplicando o SFEAP utilizando as sementes de baru.
- Analisar os parâmetros cinéticos do SFE e SFEAP, obtidos por modelagem com o modelo *Spline* e determinar o efeito da aplicação de prensagem mecânica no processo de extração supercrítica.
- Montar e validar um protótipo de extração supercrítica escala laboratório que permita operar simultaneamente a extração supercrítica com CO_2 e a prensagem mecânica a frio (sCO_2+PMF).

1.4. Estrutura do trabalho

Este trabalho está estruturado em seis capítulos, cujos conteúdos são apresentados a seguir:

No **Capítulo I** – **INTRODUÇÃO E OBJETIVOS** - São apresentados os aspectos mais relevantes para a formulação do trabalho.

No **Capítulo II** – **REVISÃO BIBLIOGRÁFICA** – são apresentados aspectos teóricos relacionados com a pesquisa do presente trabalho.

No **Capítulo III– AVALIAÇÃO DA EXTRAÇÃO SUPERCRÍTICA DA POLPA DE BURITI (*M. flexuosa*), SEMENTES DE SUCUPIRA (*P. emarginatus*) E DE BARU (*D. alata*).** Onde são apresentados os artigos:

A) Supercritical Fluid Extraction from Aguaje (*Mauritia Flexuosa*) Pulp: Overall Yield, Kinetic, Fatty Acid Profile, and Qualitative Phytochemical Profile, artigo publicado no periódico The Open Food Science Journal.
B) Technical and economic evaluation of supercritical CO_2 extraction of oil from sucupira branca seeds, artigo publicado no periódico The Journal of Supercritical Fluids.
C) A comparative and economic study of the extraction of oil from Baru (*Dipteryx alata*) seeds by supercritical CO_2 with and without mechanical pressing, artigo publicado no periódico Heliyon na seção Food Science and Nutrition.

No **Capítulo IV – EXTRAÇÃO SIMULTÂNEA COM DIÓXIDO DE CARBONO SUPERCRÍTICO E PRENSAGEM MECÂNICA A FRIO**. Onde se apresenta o artigo:

A) Simultaneous integration of supercritical fluid extraction and mechanical cold pressing for the extraction from Baru seed, artigo publicado no periódico The Journal of Supercritical Fluids.

No **Capítulo V – DISCUSSÕES GERAIS –** É apresentado uma discussão integrada dos resultados obtidos no Capítulo III e IV.

No Capítulo VI – CONCLUSÕES GERAIS. São apresentadas as conclusões gerais dos resultados obtidos utilizando os métodos SFE, SFEAP e sCO_2+PMF.

CAPÍTULO II: *Revisão Bibliográfica*

2.1. Aspectos gerais da extração supercrítica

A tecnologia supercrítica (TS) vem encontrando muitas aplicações desde sua descoberta em 1869, feita pelo cientista irlandês Thomas Andrews. E os estudos decorrentes dessa descoberta realizados em 1879 por Hannay e Hogart, permitiram entender as propriedades destes fluidos e suas potenciais aplicações. E a partir de 1882 a TS tornou-se popular frente a outras tecnologias tradicionais, devido ao menor impacto no meio ambiente (GHOSH; CHANDRA PRADHAN, 2019). O uso mais difundido da TS é a extração de compostos bioativos, outras aplicações de maior complexidade são a cromatografia de fluidos supercríticos, reações químicas e enzimáticas em fluidos supercríticos, nucleação supercrítica de fluido, processamento de polímeros/monômeros (MCHUGH; KRUKONIS, 1994).

As diversas aplicações da TS, deve-se às propriedades termodinâmicas dos fluidos em estado supercrítico. O fluido supercrítico (FS) é um estado em que a diferença entre as fases de líquido e vapor coexistentes desaparece, para um fluido puro, esta condição é adquirida quando sua pressão e temperatura alcançam ou excedem a temperatura e pressão critica (Tc e Pc, respectivamente) (KIRAN; DEBENEDETTI; PETERS, 2000). No estado supercrítico, a densidade do fluido semelhante ao líquido pode transformar-se a uma densidade semelhante ao do vapor, ajustando a pressão ou a temperatura, sem observar câmbio de fase. Uma característica interessante e bem particular do FS, é a facilidade de manipular mais suavemente a densidade ajustando a temperatura ou a pressão acima do ponto crítico. Alguns FS reportados na literatura compreendem ao metano, etano, dióxido de carbono, água, propano, etileno, propileno, metanol, etanol e acetona, cada um com propriedades críticas particulares (KIRAN; DEBENEDETTI; PETERS, 2000; POLING; PRAUSNITZ; O'CONNELL, 2001).

O dióxido de carbono supercrítico (sCO_2), é o solvente mais amplamente utilizado em várias aplicações, principalmente no processamento de alimentos funcionais, elaboração de produtos farmacêuticos, produção de aromas, sabores, óleos e gorduras. A popularidade da extração com sCO_2, deve-se essencialmente ao baixo consumo de energia, menor tempo de operação, alto rendimento, à facilidade da remoção do solvente do extrato alvo, às propriedades eco amigáveis do solvente (GHOSH; CHANDRA PRADHAN, 2019). O sCO_2 é apolar o que permite extrair apenas compostos afins, mas também compostos polares podem ser extraídas modificando-se a polaridade do solvente de extração, isto se faz, em geral, empregando água ou/e etanol (FERNANDES *et al.*, 2019; TOURNOUR *et*

al., 2015), ambos também considerados solventes eco amigáveis. Outras inovações no processo de extração com sCO_2, são a aplicação de ultrassom (SANTOS *et al.*, 2016b) e prensagem a frio (JOHNER; HATAMI; MEIRELES, 2018), os quais serão descritos com mais detalhe a seguir.

2.2. Extração de bioativos por SFE

A extração supercrítica com CO_2 foi amplamente aplicada para extração de uma enorme variedade de compostos bioativos, como lipídios de leveduras (DUARTE *et al.*, 2017), carotenoides de algas de água doce (FABROWSKA *et al.*, 2016), óleo de algas marinhas (PATIL *et al.*, 2018), óleos essenciais (CIARLINI; MARANGONI; BOLZAN, 2017), pigmentos naturais de vegetais (FATHORDOOBADY *et al.*, 2016; GARCIA-MENDOZA *et al.*, 2017), oleorresina (DEVANI *et al.*, 2020), óleo de rã (PERINA *et al.*, 2018), óleo comestível de sementes de *Psidium guava* (NARVÁEZ-CUENCA *et al.*, 2020), entre outras. Com frequência o SFE é empregado para a extração de compostos específicos, como por exemplo, a extração de cumarinas (MEDEIROS-NEVES *et al.*, 2020), timol (MORSY, 2020), cucurbitacina E (LIU; OU; GREGERSEN, 2020), amidas (LIMA *et al.*, 2020), entre outros compostos.

Nos estudos relatados no parágrafo anterior, o rendimento de extração global ou o rendimento de extração de um composto específico é usualmente avaliado tomando em conta parâmetros relacionados ao solvente de extração (tipo de solvente, concentração de co-solventes e relação S/F (g de CO_2/g matéria-prima)), a matéria-prima (tamanho de partícula, densidade aparente e porosidade) e as condições de operação da extração (temperatura, pressão, vazão do CO_2). Especial atenção foi dada à temperatura e pressão do solvente de extração, manipulando estes dois parâmetros termodinâmicos é possível regular a densidade, viscosidade e difusividade do sCO_2. Essas propriedades termodinâmicas determinam o poder de solvatação do sCO_2, e, portanto, a solubilidade do composto alvo. Sabe-se que o componente majoritário dos extratos determina em grande parte o grau da solubilidade do extrato, como foi observado no óleo de sementes de *Passiflora edulis* Sims, onde a solubilidade esteve definida principalmente pelos ácidos graxos que foram os compostos majoritários (DOS SANTOS *et al.*, 2019). No geral, é observado que o acréscimo da pressão e temperatura de extração supercrítica incrementa a solubilidade do extrato ou do composto alvo, mas um fenômeno contrário, denominado solubilidade retrograda, pode ser observado em certas condições de pressão e temperatura, produzido pela perda de poder de solvatação do sCO_2 devido à variação da pressão de vapor do soluto

(NATOLINO; DA PORTO, 2019; VILLANUEVA-BERMEJO *et al.*, 2019; BOUAZZAOUI *et al.*, 2018).

2.3. Modelagem matemática da extração supercrítica

No processo de extração supercrítica diversos modelos foram desenvolvidos para representar adequadamente o mecanismo de transferência de massa em diferentes matérias-primas (Tabela 2.1), procurando uma apropriada representação matemática (HUANG; SHI; JIANG, 2012; HATAMI; MEIRELES; CIFTCI, 2019; HATAMI *et al.*, 2020). Os modelos matemáticos desenvolvidos podem ser agrupados como: 1) modelos teóricos relativamente simples, como o modelo da teoria da camada limite (DLT), modelo de dessorção e modelo de coeficiente de partição, 2) modelo de difusão de esfera quente, 3) modelo de células quebradas e intactas (BIC) e 4) modelo de encolhimento (HUANG; SHI; JIANG, 2012).

O modelo da teoria da camada limite (DLT), considera que o processo dinâmico de extração é composto por dois processos simultâneos, transporte do composto alvo da matriz vegetal para o solvente de extração por dissolução e descarga do analito alvo do leito de extração pelo solvente de extração. De acordo com a primeira lei de Fick, um mecanismo de camada limite de difusão pode assumir o controle da dissolução do composto alvo no solvente de extração. A taxa de dissolução é dada pela Equação (1) e a concentração do composto alvo dissolvido no processo de lavagem pode ser expressa pela Equação (2).

$$\frac{dm_t}{dt} = \frac{4\pi R^2 D_e}{h}(c_{sat} - c) \qquad (1)$$

Onde, $\boldsymbol{m_t}$: massa do soluto (g), $\boldsymbol{dm_t/dt}$: taxa de dissolução, $\boldsymbol{h}$: espessura da camada de difusão, $\boldsymbol{R}$: raio das partículas sólidas (m), $\boldsymbol{D_e}$: difusividade efetiva do soluto (m^2/s), $\boldsymbol{c_{sat}}$ e $\boldsymbol{c}$: concentrações do soluto dissolvido em equilíbrio com uma superfície sólida e a massa do solvente de extração. E, temos também que:

$$\frac{dc}{dt} = \frac{F}{V}(c_0 - c) \qquad (2)$$

Onde, F: vazão volumétrica do fluido de extração (m^3/s), V: volume vazio da câmara de extração (m^3), c_0: concentração do soluto no início da extração.

Modelo de dessorção, este modelo presume que o processo de extração supercrítica possa ser tratado como dessorção do composto alvo da matriz sólida, este modelo pode ser derivado a partir de equações diferenciais, para o balanço de massa para a fase fluida (Equação 3) e o balanço de massa para a fase sólida (Equação 4) (TAN; LIOU, 1989).

$$\frac{\partial y}{\partial t} + u\frac{\partial y}{\partial z} = -\frac{1-\varepsilon}{\varepsilon} * \frac{\rho_s}{\rho_f} * \frac{\partial x}{\partial t} \quad (3)$$

$$(1-\varepsilon)\rho_s \frac{\partial x}{\partial t} = -k_d x \quad (4)$$

Onde, y: concentração do analito no solvente na fase fluida (g soluto/g solvente), x: concentração do analito na fase sólida (g soluto/g do leito sólido livre de soluto), ρ_f: densidade do solvente de extração (g/cm^3), ρ_s: densidade do leito de extração (g/cm^3), ε: porosidade do leito de extração, u: velocidade superficial do solvente (m / s), z: posição axial (m), k_d: constante da taxa de dessorção (s^{-1}).

Modelo do coeficiente de partição, foi desenvolvido utilizando o coeficiente termodinâmico de partição (K_p), definido como a concentração do composto alvo na matriz sólida que está em equilíbrio com a fase de CO_2 supercrítico. Este modelo pressupõe que a etapa inicial de dessorção e a partição subsequente de matriz-fluido são rápidas, e, portanto, não afetaria significativamente a taxa de extração. A massa do soluto em cada unidade de massa do fluido de extração pode ser calculada pelo valor K_p, e a seguir a curva de extração pode ser obtida pela Equação (6) (KUBÁTOVÁ *et al.*, 2002).

$$K_p = \frac{x}{y} \quad (5)$$

$$\frac{m_b}{m_0} = \frac{1 - \frac{m_a}{m_0}}{\frac{K_P \Delta m}{\left[(V_b - V_a)\rho_f\right] + 1}} + \frac{m_a}{m_0} \quad (6)$$

Onde, m_a e m_b são as massas cumulativas (g) de soluto extraído após o volume de extração V_a e V_b (m^3), respectivamente. Os m_a/m_0 e m_b/m_0 são as frações acumuladas do analito extraído pelo fluido de extração num volume V_a e V_b, respectivamente. Δm é a massa da amostra.

Modelo de difusão de uma esfera quente, este modelo trata o processo de extração SFE analogamente como a transferência de calor, considerando as partículas como esferas quentes esfriando num ambiente uniforme e se presume que a concentração do analito no solvente seja próximo a zero. O balanço de massa através de uma superfície interna de partículas de raio r (m), de acordo com a lei de Fick, para uma densidade e difusividade constante nas coordenadas sólidas e esféricas (r, θ e φ) pode ser expressada como se mostra na Equação (7) (REVERCHON; DONSI; OSSÉO, 1993).

$$\rho_M = -c_{s_0} D_e \left[\frac{1}{r^2} \frac{\partial(r^2 x_r)}{\partial r} + \frac{1}{r \sin\theta} \frac{\partial(x_\theta \sin\theta)}{\partial \theta} + \frac{1}{r \sin\theta} \frac{\partial(x_\varphi)}{\partial \varphi} \right] \qquad (7)$$

Onde, $\boldsymbol{\rho_M}$ é a densidade de fluxo de massa de soluto por unidade de área (g soluto/(m^2s)), $\boldsymbol{c_{s0}}$ é a concentração inicial de soluto na matriz sólida (g/m^3), $\boldsymbol{x_r}$, $\boldsymbol{x_\theta}$ e $\boldsymbol{x_\varphi}$ são as concentrações adimensionais, funções do tempo de extração, ao longo das coordenadas $\boldsymbol{r}$, $\boldsymbol{\theta}$ e $\boldsymbol{\varphi}$, respectivamente, e o $\boldsymbol{D_e}$ é o coeficiente de difusão efetivo em um substrato sólido (m^2/s).

O modelo de células quebradas e intactas (BIC), este modelo é aplicável para descrever a extração supercrítica de matéria-primas moídas, na qual o composto alvo (ou o extrato extraível) se encontra na superfície das partículas e no interior das células das partículas, se supõe que a primeira é extraída com facilidade nas primeiras etapas da extração, a seguir o composto alvo que se encontra nas células intactas das partículas da matéria-prima. A transferência de massa de acordo com este modelo pode ser derivada do balanço diferencial de massa, obtido tanto da fase sólida (matéria-prima) e fluida (solvente de extração), como se mostra nas Equações (8) e (9), respectivamente (SOVOVÁ, 1994):

$$-\rho_s(1-\varepsilon)\frac{\partial(x)}{\partial t} = f(x,y) \qquad (8)$$

$$\rho_f u \frac{\partial y}{\partial z} + \rho_f \varepsilon \frac{\partial y}{\partial t} = f(x,y) \qquad (9)$$

Onde, *f(x, y)* é a taxa de transferência de massa interfacial.

Modelo de encolhimento, descreve a extração supercrítica em duas etapas, inicialmente uma dessorção irreversível seguida pela difusão no sólido poroso através dos poros da matéria-prima. Considerando uma dispersão axial, o balanço de massa diferencial do soluto na fase do fluido se mostra na Equação (10) (GOTO; ROY; HIROSE, 1996):

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial z} = D_l \frac{\partial^2 c}{\partial z^2} - \frac{1-\varepsilon}{\varepsilon}\frac{3k_f}{R}[c - c_i(R)] \qquad (10)$$

Onde, $\boldsymbol{D_l}$ é o coeficiente de dispersão axial do soluto (m^2/s), $\boldsymbol{c_i}$ é a concentração de soluto nos poros das partículas (g/m^3), $\boldsymbol{c_i(R)}$ é a concentração do soluto nos poros na superfície da partícula, $\boldsymbol{\varepsilon}$ é a porosidade do leito, incluindo a porosidade intrínseca das partículas.

Os modelos descritos, são significativos e representam adequadamente o processo de extração supercrítica, já que são desenvolvidos por equações diferenciais de balanço de massa para leito sólido compactado, apresentando uma forma matemática diferente devido as diferentes premissas adotadas para sua solução analítica. A solução analítica dessas equações é baseado em premissas que envolvem a interação soluto – matriz sólida e a dispersão axial (HUANG; SHI; JIANG, 2012).

Modelo Spline (MEIRELES, 2008), é um modelo empírico empregado para modelar a curva de extração global (CEG). A curva CEG é construída plotando o rendimento acumulado do extrato versus o tempo de extração. Esta curva fornece informação do tempo de extração necessário para um lote de matéria-prima. Uma curva típica da CEG possui três períodos; 1) Um período com taxa de extração constante, chamado de período CER (siglas em inglês para *constant extraction rate*), 2) Um período de queda da taxa de extração, chamado de período FER (siglas em inglês para *falling extraction rate*), y 3) Um período onde a extração do analito é controlada por difusão, chamado de período DC (siglas em inglês para *Diffusion-controlled rate period*). O modelo *spline* descreve adequadamente os períodos da CEG, ajustando os dados experimentais do rendimento de extração (massa do extrato) versus o tempo, usando a equação geral do modelo para $\boldsymbol{N}$ linhas:

$$m_{Ext} = \left(b_0 - \sum_{i=1}^{i=N} C_i b_{i+1}\right) + \sum_{i=1}^{i=N} b_i t \qquad (11)$$

Onde; $\boldsymbol{b}$ são os coeficientes lineares das linhas, $\boldsymbol{C}$ são as interceptações dessas linhas, $\boldsymbol{m_{Ext}}$ é a massa do extrato e $\boldsymbol{t}$ é o tempo.

Tabela 2.1. Algumas aplicações de modelos matemáticos em diferentes matérias-primas.

Modelo	**Matéria prima**	**Tipo de extrato**	**Compostos**	**Ref.**
Equações diferenciais parciais (EDP) baseado na transferência de massa.	Sementes e pele de tomate	Oleoresina	Licopeno	HATAMI; MEIRELES; CIFTCI, (2019)
Modelo de células quebradas e intactas	Sementes de *Punica granatum* L.	Óleo	Ácidos graxos	NATOLINO; DA PORTO, (2019)
Modelo de difusão de uma esfera quente	*Genipa americana* L.	Extrato	Ácidos graxos e genipina	NÁTHIA-NEVES *et al.*, (2020)
Modelo empírico Modelo Spline Modelo logístico Modelo de difusão	Subproduto de arroz	Óleo	γ-orizanol	JESUS *et al.*, (2013)

2.4. Inovações no processo SFE

2.4.1. SFE assistido por ultrassom

Na literatura disponível mais recente sobre este método, duas configurações do dispositivo de ultrassom na unidade de extração supercrítica são relatadas. A primeira consiste em um banho de ultrassom, na qual é submersa a coluna de extração, este método foi aplicado para a recuperação de bioativos das sementes de *Iberis amara*, obtendo-se um incremento do rendimento de extração em 26,1 % com respeito a SFE, com uma diminuição do tempo de extração em 34,8% e uma redução de uso de CO_2 em 52% (LIU; OU; GREGERSEN, 2020). Na segunda configuração, o ultrassom foi aplicado com uma sonda introduzida no interior da coluna de extração, os autores do estudo reportaram que houve um incremento da taxa de extração de ácidos graxos do óleo de sementes de baru, mas o rendimento global e o perfil de ácidos graxos final, foram similares aos obtidos pelo método SFE (SANTOS *et al.*, 2016). A extração supercrítica assistida por ultrassom é uma

alternativa interessante para extração de bioativos de alto valor biológico, mas a sua implementação em escala maior é um desafio atual.

2.4.2. SFE assistido por prensagem a frio (SFEAP)

O SFEAP, nas suas siglas em inglês significam *Supercritical fluids extraction assisted by pressing*, é um novo método de extração que combina a extração supercrítica convencional (SFE) e a prensagem a frio. Recentes aplicações na extração de óleo de *Caryocar brasiliense* (JOHNER; HATAMI; MEIRELES, 2018), óleo volátil de botões de cravo (HATAMI *et al.*, 2019) e óleo volátil de sementes de funcho (HATAMI; JOHNER; MEIRELES, 2018), mostram que a implementação da prensagem a frio resultou num incremento do rendimento de extração. A Tabela 2.2 mostra o rendimento final obtido no final da cinética de extração em condições ótimas de pressão e temperatura, ambas determinadas para os métodos SFE e SFEAP. Embora o rendimento final para a polpa de pequi pelo SFEAP não seja muito superior ao SFE, observou-se que a taxa de transferência de massa no período CER para o SFEAP (9,10 min^{-1}) foi superior ao SFE (2.87 min^{-1}). E o t_{FER} do SFEAP (21,44 min) foi menor do que o SFE (29,7 min), nesses períodos de tempo é possível extrair 80% (SFEAP) e 75% (SFE) do óleo extraível em cada método.

Tabela 2.2. Estudos comparativos de cinéticas SFE v.s. SFEAP.

Matéria prima	Método	Pressão (MPa)	T (°C)	TE (min)	Vazão (g CO_2/min)	S/F	Y (%)	Ref.
Polpa de pequi	SFE	40	60	200	17,58	352	53,4	[1]
	SFEAP	40	60	200	17,58	352	55	
Funcho	SFE	20	40	-	-	95	9,8	[2]
	SFEAP	20	40	-	-	95	12,2	
Botões de cravo	SFE	15	40	14	6,34	7,4	21,3	[3]
	SFEAP	15	40	14	6,34	7,4	22,2	

T: temperatura, TE: tempo de extração, S/F: razão g CO_2/g matéria-prima, Y: rendimento de extração

[1]JOHNER; HATAMI; MEIRELES, (2018)

[2]HATAMI; JOHNER; MEIRELES, (2018)

[3]HATAMI *et al.*, (2019)

Na extração de óleo volátil de funcho, observou-se um incremento substancial no rendimento de extração de 24,5% em relação ao SFE aplicando-se o método SFEAP, o que torna atrativo o acoplamento da prensagem a frio ao processo de extração para essa matéria-prima (HATAMI; JOHNER; MEIRELES, 2018). Na extração de óleo volátil de botões de cravo aplicando SFEAP obteve-se um incremento no rendimento de apenas 4,23% em relação ao método sem prensagem, a avaliação econômica da aplicação desse método para extração de óleo volátil de cravo permitiu verificar a viabilidade técnica e econômica para implementação a escala industrial (HATAMI *et al.*, 2019).

As vantagens da implementação da prensagem a frio no processo de extração supercrítica são vantajosas em termos econômicos e técnicos (HATAMI *et al.*, 2019), mas o fato de que a prensagem seja executada como uma etapa prévia à extração supercrítica, o que resulta num gasto adicional de energia e tempo de operação, isto pode ser traduzida em desvantagens operacionais do processo de extração. Na literatura científica atual disponível não existe nenhum resultado sobre a operação simultânea do método de prensagem a frio e do método de extração supercrítica com dióxido de carbono, acredita-se que o funcionamento simultânea destes dois métodos permitirá aprimorar o processo de extração supercrítica por SFEAP.

2.4.3. GAME

GAME são siglas em inglês para o método *Gas assisted mechanical expression*. O GAME foi desenhado para a recuperação de óleo de oleaginosas convencionais (WILLEMS; KUIPERS; DE HAAN, 2008) e não convencionais (sementes de uvas) (ROMBAUT *et al.*, 2014). O equipamento para a execução do método GAME dos dois estudos tiveram configuração e forma de operação diferentes. O equipamento GAME para a obtenção do óleo das sementes de uvas apresenta um pistão móvel deslocado com o auxílio de um líquido hidráulico (água), a pressão mecânica exercida é constante durante o processo de extração supercrítica com dióxido de carbono a 104 ºC (ROMBAUT *et al.*, 2014). Uma proposta anterior do GAME, foi feita utilizando uma prensa hidráulica com uma pressão máxima de até 100 MPa, mais detalhes técnicos do equipamento podem ser revisados no artigo da referência (WILLEMS; KUIPERS; DE HAAN, 2008). As sementes de gergelim, linhaça, colza, palmiste e jatropha, são as oleaginosas convencionais submetidas a extração com o GAME, os rendimentos obtidos foram maiores em 30% m/m do que a extração por prensagem hidráulica (WILLEMS; KUIPERS; DE HAAN, 2008). O

GAME é um método interessante para a recuperação de óleos comestíveis, mas a qualidade fitoquímica dos óleos não foram estudados em relação as condições de operação, especialmente em temperatura elevadas.

CAPÍTULO III: *Avaliação da Extração Supercrítica de Polpa de Buriti (Mauritia flexuosa), Sementes de Sucupira (Pterodon emarginatus) e de Baru (Dipteryx alata)*

Artigo 1: **Supercritical Fluid Extraction from Aguaje (*Mauritia Flexuosa*) Pulp: Overall Yield, Kinetic, Fatty Acid Profile, and Qualitative Phytochemical Profile**

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RESEARCH ARTICLE

Supercritical Fluid Extraction from Aguaje (*Mauritia Flexuosa*) Pulp: Overall Yield, Kinetic, Fatty Acid Profile, and Qualitative Phytochemical Profile

Larry Oscar Chañi-Paucar[1], Edgar Torres Yali[2], Júlio César Maceda Santivañez[3], Dina Aro Garcia[2], Júlio C F Jonher[1] and Maria Angela A Meireles[1,*]

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Abstract:

Aims:

This work aims to understand the effects of processing variables on supercritical fluid extraction from *Mauritia flexuosa* (Aguaje). This is not a cultivar because the plants used are indigenous.

Background:

The production of *Mauritia flexuosa* (Aguaje) is an economically significant activity in Madre de Dios, Peru, which has rarely been studied from a nutritional point of view.

Objective:

The present study evaluated the supercritical extraction of dry aguaje pulp (DAP).

Methods:

The supercritical extraction was evaluated at 200, 250, 300, 350, and 400 bar and temperatures of 40 and 60°C, and its effect on the global yield, fatty acid profile (FAP), and qualitative phytochemical profile (QPP). The kinetics data were fitted to the Spline model. The FAP was determined by gas chromatography, and the QPP was determined by thin-layer chromatography.

Results:

The highest yield (51.5 g extract/100 g DAP) was observed at 400 bar and 60°C in 79 min of extraction and 8.6 g CO_2/min. The spline model showed that it is possible to extract 87.8% (45.2 g extract/100 g DAP) of the total extract in the t_{FER} (falling rate period) period (38.99 min). The fatty acid and bioactive compound profiles were not affected qualitatively by the different extraction conditions.

Research perspectives:

The extracts obtained in this work were further studied with respect to the formation of emulsions, the development of cosmetics, and food supplements.

Conclusion:

DAP's supercritical extraction was carried out successfully, obtaining a high-quality phytochemical extract with potential applications in functional foods, drugs, and cosmetics.

Keywords: Aguaje pulp, Supercritical fluid extraction, Edible oil, Fatty acids, Phytochemicals, Mauritia flexuosa.

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1. INTRODUCTION

Mauritia flexuosa is a palm tree species distributed throughout the Amazon region of Bolivia, Brazil, Colombia, Ecuador, French Guiana, Guyana, Suriname, Trinidad-Tobago, Venezuela, and Peru [1]. In Peru, the palm and fruit are known under the name "Aguaje"; the cities of Iquitos and Loreto are often reported as the most significant producers [2, 3]. However, other cities in Peru, such as Madre de Dios, have an important but little-known production. The production is derived from natural plantations with or without association with conventional crops such as palm trees.

The pulp of Aguaje from Madre de Dios is popularly known for its high lipid content, but there are no scientific studies that evaluated the lipid profile of the fruits of this region. Proximal analysis of Aguaje from other regions of the Peruvian Amazon has reported the following values for pulp + shell: humidity of 54.4%, fiber content of 10.1%, the lipid content of 18.1%, the ash content of 1.2%, the protein content of 2.3%, and carbohydrate content of 13.9% [4]. Aguaje oil has captured researchers' interest for its content in fatty acids, carotenoids, tocopherols, tannins, and flavonoids [5, 6]. Recent research shows interesting results of the application of Aguaje oil in the elaboration of functional foods [7] as a protector against the mutagenic effects of drugs used in cancer chemotherapy [8] in the manufacture of photoprotective creams and lotions [9, 10]. Therefore, new applications of Aguaje oil is obtained through clean and safe processes, which does not present potential health risks.

Although the extraction of lipids with organic solvents is efficient [11, 12], there is a potential risk to human health, for instance, cancer and other diseases, due to traces of these toxic solvents and the possible reactions that can trigger ethereal extracts. Cold mechanical extraction presents variable yields depending on the extraction temperature [4, 11]. Furthermore, the extraction is not selective; then, filtering and neutralization operations with NaOH are necessary. On the other hand, the method of supercritical fluid extraction (SFE), especially with CO_2, applied to the extraction of pulps from oleaginous fruits allows high yields of high-quality extracts to be obtained without potentially harmful organic solvent residues. SFE with or without cosolvent depends on the process temperature, pressure, and amount of cosolvent; the kinetics of the process depends on the CO_2 flow, particle size, and solvent mass/feed mass (S/F) [13 - 15].

In the search for the scientific literature available in the SCOPUS and Web of Science databases, using no restrictions and the term "Supercritical fluids extraction *Mauritia flexuosa*," only one article describing the Aguaje oil extraction by SFE was found [5]. This study focused mainly on the extraction of carotenoids, noting that the most considerable fraction of the pigment was extracted with the oil in the diffusion-controlled step, which shows that a complete recovery of the oil is necessary. These authors reported an efficient oil extraction (~ 7.5 g oil/100 g sample) at 300 bar and 40°C, using a 95 min time, flow rate of 18.4 g CO_2/min, and an S/F of 24. The effect of pressure and temperature on the extraction yield is not clear, mainly because only two pressures (200 and 300 bar) were used in the assays. The solubility of lipid compounds in sc-CO_2 varies with both temperature and pressure, directly affecting the lipid compounds' vapor pressure and the density of CO_2 (therefore, its solvation power) [16]. As Aguaje oil is a complex mixture of compounds [5, 11] and aiming at complete extraction, it is pertinent to evaluate the effect of pressure on the extraction yield in shorter pressure intervals (every 50 bar).

Aguaje oil has a significant amount of fatty acids, predominantly unsaturated fatty acids [4, 11]. There is no report in the literature on the effect of SFE conditions on the fatty acid composition of Aguaje oil. For instance, Cordeiro *et al.* [17], and Ndayishimiye *et al*. [18], reported the effects of SFE conditions on the extracts of *Virola surinamensis* seed oil and citrus residues (seeds and skins), respectively.

Several properties are attributed to Aguaje oil, such as its antimicrobial activity [19], regulation of iron accumulation [20], antiplatelet and antithrombotic activities [21] and antimutagenic effect [8]. In these studies, these properties are attributed to fatty acids and carotenoids. Nevertheless, these studies are not conclusive since the oil was solely used in the activity tests, and the chemical composition profile was not addressed. Therefore, other unidentified compounds may act concomitantly, making it necessary to perform a phytochemical screening. Based on these considerations, the present study aimed to evaluate the supercritical CO_2 extraction of oil from Aguaje pulp at different pressures (200, 250, 300, 350, and 400 bar) and temperatures (40 and 60°C), analyzing the effects of these variables on the fatty acid profile and qualitative phytochemical profile.

2. MATERIALS AND METHODS

2.1. Raw Material

The fruits of Aguaje (*M. flexuosa*) were harvested from a small farmer's farm, located 5 km from Puerto Maldonado city, on the road known as "Corredor Turístico Chonta - Infierno" in the Joya District, Tambopata Province, Madre de Dios Department, Peru (Fig. **1A**). Aguaje fruits were harvested by climbing to the palm trees' top with a belt adapted for this task (Fig. **1B**). The clusters of Aguaje fruits were cut with a machete and allowed to fall to the ground (Fig. **1C**). Then, the fruits were manually removed from the bunches with the help of a machete and transported to the farmer's residence, where the fruit conditioning phase began, to obtain the dry pulp of Aguaje.

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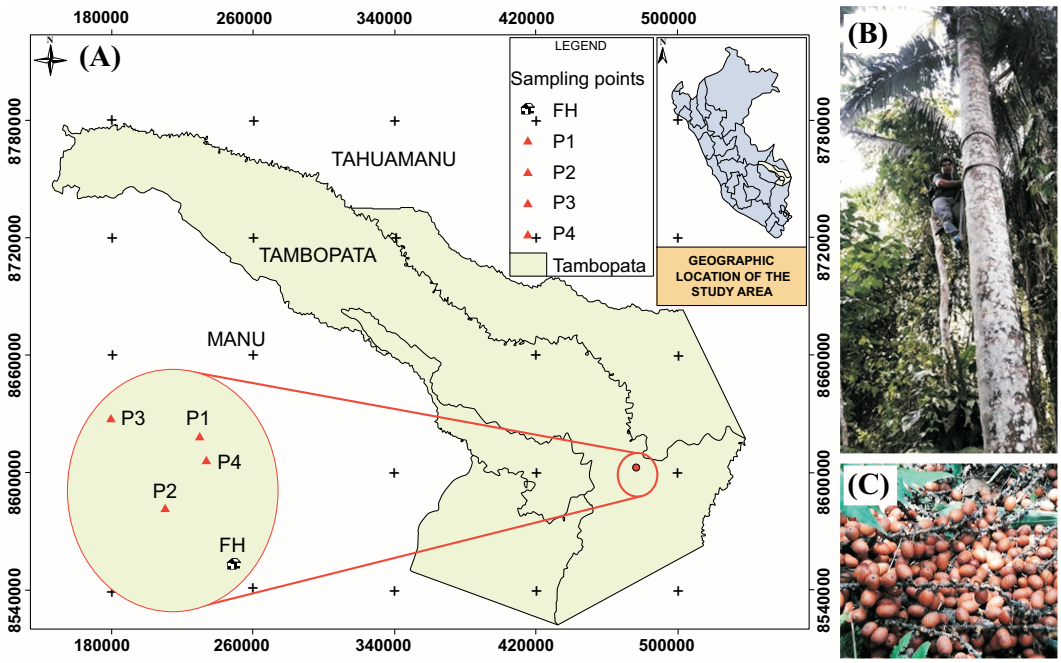


Fig. (1). Aguaje fruit harvest location map (**A**), including sampling points P1 (east 476213, and north 8602633), P2 (east 476186, and north 8602584), P3 (east 476144, and north 8602646), P4 (east 476218, and north 8602617), and the farmer's house (FH: east 476239, and north 8602545). Harvest (**B**), and fruits (**C**).

2.2. Sample Preparation

After harvesting, Aguaje fruits clean and free from debris were subjected to thermal treatment in a homemade manner. In short, the treatment was carried out by heating in an aluminum pan (Record, Peru) 24 kg of Aguaje fruits with approximately 24 liters of water until reaching a temperature between 35 and 40°C. This temperature was kept constant until the pulp was soft; this was achieved in approximately 30 minutes. The period of heat treatment was defined using two empirical criteria: the ease of manually removing the peels and the softening of the pulp. After the heat treatment, the fruits were peeled and pulped manually with a spoon's aid; the pulp was packed in polyethylene bags and stored at -20°C.

The frozen pulp was transported to the Laboratory of Agroindustrial Processes, Faculty of Agroindustrial Engineering of the National University of Madre de Dios (UNAMAD), where it was thawed at room temperature. Afterward, it was subjected to drying in an oven with air circulation at 40°C for 16 hours. These conditions were lower than those used by de França *et al*. [5], (60°C and 24 hours) to prevent thermolabile bioactive compounds' degradation. The dried pulp was packed in polyethylene bags of one kilogram and stored with protection from light at -20°C. They were transported to the Laboratory of Supercritical Technology (LASEFI), of the School of Food Engineering (FEA), of the University of Campinas (UNICAMP), São Paulo, Brazil, where subsequent data collections were carried out.

2.3. Supercritical Extraction of Oil from Aguaje Pulp

The extractions were carried out using the equipment Speed (Applied Separations, model 7071, Allentown, USA), with a micrometric valve heated by a homemade system (Fig. **2**, detail V4), composed of electrical resistance, a temperature controller, a temperature sensor and a vat containing distilled water without forced circulation, where the micrometric valve body was submerged, and the vat water temperature was maintained at approximately 55 ± 2°C. The cooling bath temperature was constant at -2 ± 1°C for cooling the pneumatic CO_2 pump head (Fig. **2**, detail 3).

The extraction experiments were carried out, combining temperatures of 40 and 60°C with pressures of 200, 250, 300, 350, and 400 bar, for a total of 10 assays. Approximately 23 g of dry Aguaje pulp (DAP) was used for each extraction; this mass amount allowed the complete filling of the 25 mL stainless steel extraction column. After packaging the sample and installing the extraction column in the equipment, the blocking valve (Fig. **2**, detail V1) of the CO_2 cylinder (99.9% pure, White Martins, Campinas, Brazil) was opened. The blocking valve located immediately before the extraction column (Fig. **2**, detail V2) was also opened, maintaining the extraction column outlet blocking valve (Fig. **2**, detail V3) closed; this last valve remained closed for 10 minutes; this period is denoted as static time. After the static time (10 min), the extraction column outlet blocking valve (Fig. **2**, detail V3) was opened, starting the dynamic extraction period that lasted 38 minutes. The CO_2 mean flow rate was maintained at 8.9 g/min and manually regulated with the micrometer valve (Fig. **2**, detail V4). The extract was collected in 100 mL glass flasks protected from light with aluminum foil. After the extraction was completed, the flasks were closed and stored at -20°C until the analyses were performed.

The effect of the extraction conditions was assessed by determining the OEY (g extract/100 g DAP) with Equation 1: where OEY is the overall extraction yield; m_{oil} is the mass of

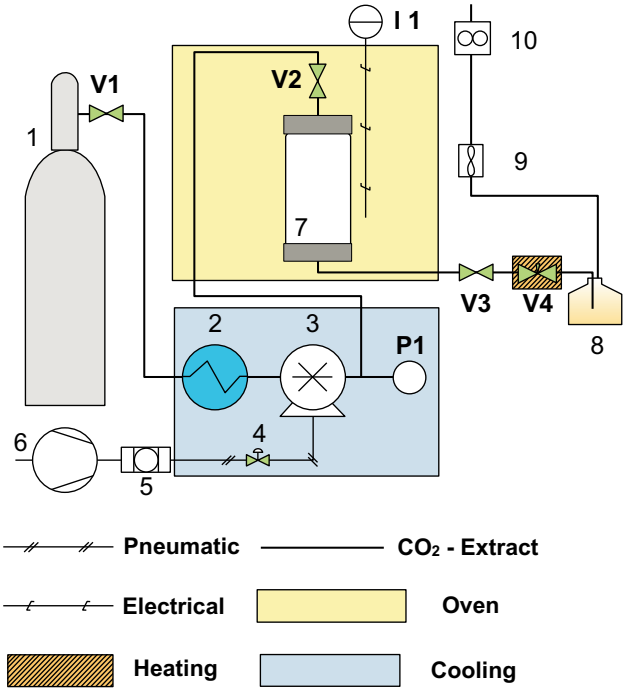
the extract in grams; and m_{DAP} is the mass of the DAP used for extraction in grams.

$$OEY(g\ extract/100g\ DAP) = \frac{m_{extract\ (g)}}{m_{DAP\ (g)}} \times 100 \quad (1)$$

2.4. Extraction Kinetics

The kinetic extraction curve was constructed by plotting the accumulated extraction yield (g extract/100 g DAP) versus the extraction time (min). The extraction was carried out with approximately 23 g. DAP under pressure and temperature conditions that obtained the best performance, as determined in the previous assays. The extraction had an approximate duration of 79 min. This time does not include the static period, which had a duration of 10 min. During the dynamic extraction, eighteen collections were made to build the extraction kinetics. The mathematical modeling of the experimental data was performed using the model described by Meireles [22], which describes that typically the overall extraction curve (OEC) presents three different regions with different extraction rates. Initially, a period of constant extraction rate (CER) is established in which the extract contained on the surface of the particles is removed mainly by convection. The following region is characterized by a period of falling extraction rate (FER) in which extraction is carried out by convection and diffusion. Finally, a period controlled by diffusion (DC) is established.

The mathematical spline model is shown in Equation 2, where m_{Ext} is the extraction yield (g extract/100 g DAP); a_1, a_2 and a_3 are slope coefficients (first-order terms) of the straight lines CER, FER and DC, respectively (min^{-1}); t_{CER} is the time interval of the CER period (min); and t_{FER} is the end of the FER period (min).



1	CO_2 reservoir	9	Flowmeter
2	Cooling bath	10	Flow totalizer
3	Air-driven CO_2 pump	I1	Temperature Indicator
4	Control (air pressure)	P1	Pressure gauge
5	Air filter	V1	Blocking valve
6	Air compressor	V2	Blocking valve
7	Extraction cell	V3	Blocking valve
8	Extract collecting vessel	V4	Micrometering valve

Fig. (2). Schematic diagram of the supercritical extractor. (Applied Separations Inc, Allentown, USA).

$$m_{Ext} = a_1 t; \qquad t \leq t_{CER} \qquad \textbf{(2.a)}$$

$$m_{Ext} = a_1 t + a_2(t - t_{CER}); \qquad t_{CER} < t \leq t_{FER} \qquad \textbf{(2.b)}$$

$$m_{Ext} = a_1 t + a_2(t - t_{CER}) + a_3(t - t_{FER}); \qquad t_{FER} \leq t \qquad \textbf{(2.c)}$$

2.5. Determination of the Fatty Acids Composition

The extracts obtained under different pressure and temperature conditions were analyzed to determine their fatty acid composition. The extract was esterified to obtain fatty acid methyl esters (FAME) with approximately 0.5 g of extract, 10 mL of methanol, 2 drops of H_2SO_4, and reflux for 2 hours [23]. FAMEs were extracted with hexane and organic phase injection in an Agilent 6890 gas chromatograph. The chromatograph was equipped with a Stabilwax column (30 m × 0.25 mm; 0.25 μm) and a flame ionization detector (FID). Helium was used as the carrier gas, and the temperature was programmed as follows: at 45°C for 2 minutes, at 5°C/min up to 50°C, at 30°C/min up to 250°C, with isotherm for 10 minutes. The injector and detector temperatures were adjusted to 250°C and 280°C, respectively.

The identification of fatty acids was carried out by comparing the retention times of FAMEs obtained from Aguaje extracts with the profile of a FAME pattern (Supelco, C8-C24 p/n CRM18918, Bellefonte, PA, USA) analyzed under the same chromatographic conditions. Fatty acids were quantified by calculating the percentages of peak areas for each FAME, reporting as a relative percentage (%) [24].

2.6. Qualitative Phytochemical Characterization

The extract samples were subjected to thin-layer chromatography (TLC) analysis, according to the methodologies proposed by Wagner *et al.* [25], to show the different classes of chemical substances. Silica gel 60 chromatoplates (5 cm×5 cm, Macherey – NageL-MN®) were used, impregnated with a 0.20 mm thick UV254 nm fluorescence indicator (manganese activated zinc silicate with green fluorescence). Two lines were gently marked with 0.5 cm graphite pencil from the beginning and end of the chromatoplate, leaving 4 cm of space for the separation of chemical substances. The extracts were previously solubilized (1 part of extract:3 parts of hexane), and with the aid of a capillary tube, they were applied over the line drawn at the bottom of the chromatoplate. The chromatoplate was then placed in a glass vat containing an elution composed of hexane and ethyl acetate (9:1 v/v). The chemical substances present in the chromatoplates were developed using physical methods (ultraviolet light at wavelengths 254 and 365 nm) and chemical methods. Five developers, the anisaldehyde reagent - sulfuric acid (AS), Dragendorff reagent (DRG), ceric sulfate ($Ce(SO_4)_2$), potassium hydroxide (KOH) and ferric chloride ($FeCl_3$) were prepared according to the method proposed by Wagner and Bladt [26] and Wagner *et al*. [25], with some modifications that are detailed below:

The AS reagent was prepared by mixing 0.5 mL of anisaldehyde, 10 mL of glacial acetic acid, 85 mL of methanol, and 5 mL of concentrated sulfuric acid. Flavonoids, terpenes, fatty acids, iridoids, and sugars emit colors between red-violet in visible light and UV-365 nm after heating the chromatoplates sprayed with the developer.

Ferric chloride ($FeCl_3$) was prepared by dissolving 3 g of $FeCl_3$ in 100 mL of ethyl alcohol. Aromatic compounds are visible after spraying the reagent.

DRG was prepared by mixing two solutions. The first solution (I) was prepared by dissolving 0.85 g of basic bismuth nitrate in 10 mL of glacial acetic acid under heating; this solution was added to 40 mL of distilled water. The second solution (II) was prepared by dissolving 8 g of potassium iodide in 20 mL of distilled water. The two solutions were mixed; 5 mL of solution I with 5 mL of solution II, and 20 mL of acetic acid were added, followed by the addition of distilled water to complete 100 mL. Alkaloids, heterocyclic nitrogen compounds, and quaternary amines are detectable in visible light on chromatoplates sprayed with this developer.

KOH was prepared by dissolving 1 g of KOH in 100 mL of ethanol. The chromatoplate sprayed with this developer was evaluated under visible light and UV-365 nm without heating. The detectable compounds are anthraquinones (red), anthrones (yellow, UV-365 nm), and coumarins (blue, UV-365 nm).

The developer Ce $(SO_4)_2$ was prepared according to Khalid *et al*. [27], and Stahl [28] with some modifications: 4.2 g of cerium sulfate IV was dissolved in 500 mL of distilled water, 2.8 mL of concentrated sulfuric acid was added and heated, and then allowed to cool. This solution was completed in 100 mL of distilled water. Terpenes, sterols, and other similar compounds show visible spots after heat treatment of the sprayed chromatoplate with this developer.

2.7. Calculation of the Kinetics Parameters

The experimental data were expressed as the average of two repetitions from the extraction assays, kinetics, and fatty acids' composition. The modeling of the extraction kinetics Equations 2.a – 2.c was performed using the genetic algorithm (GA) with MATLAB software (MathWorks, version R12). The fit quality of the experimental data to the Spline model was evaluated considering the objective function defined as the absolute average relative deviation (AARD) referred to the yield expressed by Equation 3 [29]:

$$\text{AARD}(\%) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}}\right| \qquad \textbf{(3)}$$

where AARD is the average absolute relative deviation (%), n is the number of data points, and $x_{i,exp}$ and $x_{i,cal}$ refer to the experimental and calculated yields for data i, respectively.

3. RESULTS AND DISCUSSION

3.1. SFE-CO_2

Table **1** shows that the OEY obtained in all experimental conditions was higher than the highest OEY (7.8 g extract/100 g DAP) reported by de França *et al*. [5], employing the same extraction method. Our results were also superior to the OEYs found in hexane extraction [12], discontinuous mechanical

pressing [4], and continuous [11]. The results obtained were superior to the OEY of extraction with petroleum benzene [11] at pressures of 350 and 400 bar for the two isotherms (Fig. **3**). The differences observed in the OEY of our study compared to those in the literature (Table **1**) are probably due to the higher solubility of the Aguaje extract achieved due to the increase in the CO_2 solvation power under the studied conditions. Additionally, the Aguaje pulp used in this study had a high lipid content compared to that reported in the literature (Table **1**). OEY at different pressure and temperature conditions was plotted against the pressure and density of the sc-CO_2 obtained in the two isotherms (Fig. **3**).

In general, at the two extraction temperatures (40 and 60°C), the OEY increased when the increase in pressure. At 40°C, the lowest extraction yield was 23.5% at 200 bar, and the highest yield was 36.2% at 400 bar. At 60°C, the lowest yield observed was 24.5% at 200 bar, and the highest yield was 41.1% at 400 bar. At the 60°C isotherms, it was observed that the extraction yield increased in the 200 to 300 bar range; a similar trend was observed for the 40°C isotherm. From 300 bar in the 60°C isotherm, the yield increased substantially up to 400 bar (Fig. **3**).

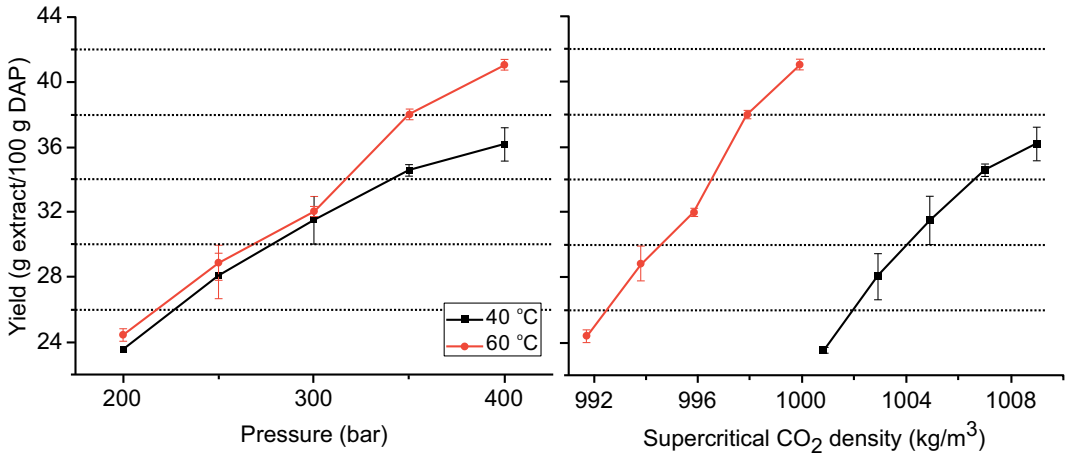


Fig. (3). Extraction yield at different pressures (200, 250, 300, 350, and 400 bar) and temperatures (40 and 60°C) with supercritical carbon dioxide.

Table 1. Current literature on supercritical, mechanical, and solvent extraction of M. flexuosa pulp and other palm trees in the Amazon.

RM	EM	SS	Pressure (bar)	Temperature (°C)	TE (min)	Flow rate (g. CO_2/min)	S/F (g/g)	Oil yield** (% mass)	Composition*	Reference
M. flexuosa	SFE-CO_2	Pará-Brazil	200 and 300	40 and 55	95 - 210	16.8 - 31.8	24 - 39	4.7 - 7.8	Carotenoids, tocopherols, and fatty acids	França *et al*. [5]
M. flexuosa	Mechanical extraction continues	Guaviare-Colombia	NR	25 - 30	-	-	-	22	Triglycerides, diglycerides, fatty acids, acylcarnitine, ceramides, ergosterol, lysophosphatidylcholine, phosphatidyl, ethanolamine, and sphingolipids	Jaramillo *et al*. [11]
M. flexuosa	Solvent extraction (petroleum benzine)	Guaviare-Colombia	-	40 - 60	NR	-	-	33		
M. flexuosa	Solvent extraction (Hexane)	Roraima-Brazil	-	NR	360	-	-	23.2	Omegas 3 (ω3), 6 (ω6) and 9 (ω9)	Santos *et al*. [12]
M. flexuosa	Mechanical extraction	Loreto-Perú	392.3	25 and 60	20	-	-	4.0 - 17.9	fatty acids	Jacobo *et al*. [4]
Mauritia aculeata	Solvent extraction (Hexane)	Roraima-Brazil	-	NR	360	-	-	26	Omegas 3 (ω3), 6 (ω6) and 9 (ω9)	Santos *et al*. [12]
Acrocomia aculeata	SFE-CO_2	Brazil	180 - 220	40 - 80	200	1.62 - 2.67[a]	19 - 31	9.3 - 41.6	Free fatty acids, phytosterol (Campesterol and β-sitosterol) and tocopherol (α, δ, and γ)	Trentini *et al*. [30]

(Table 1) contd.....

Acrocomia aculeata	Solvent extraction (n-Hexane)	Brazil	-	68	480	-	-	43.7	Free fatty acids, phytosterol (β-sitosterol) and tocopherol (α, δ, and γ)	Trentini *et al*. [30]
Oenocarpus bacaba	SFE-CO_2	Pará-Brazil	120 - 420	40 and 60	180	5.31	48	4.3 - 60.4	fatty acids	Pinto *et al*. [31]
Oenocarpus bacaba	Solvent extraction (n-Hexane)	Roraima-Brazil	-	NR	360	-	-	43.9	Omegas 3 (ω3), 6 (ω6) and 9 (ω9)	Santos *et al*. [12]
M. flexuosa	SFE-CO_2	Madre de Dios-Perú	200 - 400	40 and 60	38	8.9	14.7	23.5 - 41.1	Fatty acid Terpenoids***	Current study

RM: Raw material; EM: Extraction method; SS: Sample source; TE: Extraction time;
[a]Calculated with CO_2 density = 0.54 - 0.89 g/cm^3;
* It only reflects what the authors researched at that time;
** Mass of extract/mass of dry raw material;
***Detection of the presence of terpenic compounds by TLC.

The OEY observed in this study showed the expected behavior when pressure and temperature increased (Fig. **3B**) because these two parameters modify the density and other properties of CO_2 (solvent): The increase in CO_2 solvation power is due to the increase in the density, while the vapor pressure of the extract decreases, facilitating solubilization [16, 31, 32]. The increase in the CO_2 density contributes to the increase in the DAP extract's solubility in the solvent, which led to an increase in the OEY (Fig. **3B**). There was a small increase in the OEY (between 1.7 and 3.9%) in the pressure range of 200 - 300 bar as the temperature increased from 40 to 60°C (Fig. **3**). At 300 bar, the OEY was equal as the temperature increased from 40 to 60°C (32±2 and 32±0.3%, respectively); therefore, the phenomenon known as retrogradation is detected at this pressure. Bouazzaoui *et al.* [33], observed this same phenomenon in the extraction of oil from *Cucumis melo* seeds at 700 bar for a similar temperature variation (40 to 57°C). This retrogradation pressure was higher than that observed in our study, which was probably due to the difference in the composition of fatty acids in *C. melo* oil (68.2% polyunsaturated fatty acids) and Aguaje oil. At pressures of 350 and 400 bar, increasing the temperature (40 to 60°C) led to a substantial increase in the OEY (Fig. **3**). A similar effect was reported for the *Virola surinamensis* extraction study at 350 bar and 40 to 80°C [17], *Oenocarpus bacaba* at 420 bar and 40 to 60°C [31] and *Aleurites moluccana* at 350 bar and 40 to 60°C [34]. Cunha *et al*. [14], reported a different behavior for SFE from *Oenocarpus distichus Mart.*, registering an increase in OEY of less than 1% as the temperature increased from 50 to 60°C in the pressure range from 350 to 420 bar. This behavior allowed us to infer that variations in solubility due to the variation in temperature and pressure in the studied ranges did not change *O. distichus* oil's extraction yield in CO_2, which did not occur in our study.

3.2. Spline Model

The kinetic parameters were obtained by fitting the OEC (Fig. **4**, 400 bar and 60°C) to the spline model. The kinetics were evaluated for a maximum period of 79 min, reaching an S/F ratio of 29 and an accumulated yield of 51.5 g extract/100 g DAP. The kinetic curve showed three periods with different extraction rates, which are well represented by the spline model's three straight lines, as shown in Fig. (**4**). The model was adequately fitted to the experimental data according to the calculated AARD value, which was less than 10%; this value is within the range recommended by other authors [29]. According to Meireles [22] and Jesus *et al*. [35], the first straight line with an inclination of 4.1047 min^{-1} (Table **2**) predominates a period of extraction at a constant rate (CER), obtained by convection of the extract of easy access that involves the solid particles of DAP. The following straight line, with a slope of 0.7498 min^{-1} (Table **2**), shows a period of decreasing extraction rate (FER). In this period, the extraction is carried out by both convection and diffusion. The last straight line, with a slope of 0.1635 min^{-1} (Table **2**), represents the period in which the extraction rate is controlled by diffusion (DC).

The curve's constants with three straight lines obtained by the Spline model are shown in Table **2**, and in t_{FER} (39.0 min), 45.2 g extract/100 g DAP was obtained, which is approximately 87.8% of the total extractable substances. A different situation was reported by de França *et al*. [5], who reported a yield of 6.8 g extract/100 g DAP in the t_{CER} (53.6 min) at 300 bar and 40°C. These differences can be explained by the higher temperature and pressure used in the present study, obtaining a higher yield (Fig. **4**). The results are promising for projects to scale up the process due to the high yield obtained and a lower CO_2 flow rate (Table **1**) used in this study with respect to that reported in the consulted literature.

Table 2. Numeric values of the Spline model constants for 400 bar and 60°C.

Extraction method	Constant						ARRD (%)
	a_1	a_2	a_3	t_{CER}	t_{FER}	t_{total}	
SFE-CO_2	4.1047	0.7498	0.1635	4.77	38.99	79	8.32
a_1, a_2 and a_3 (min^{-1}); t_{CER}, t_{FER}, and t_{total} (min).							

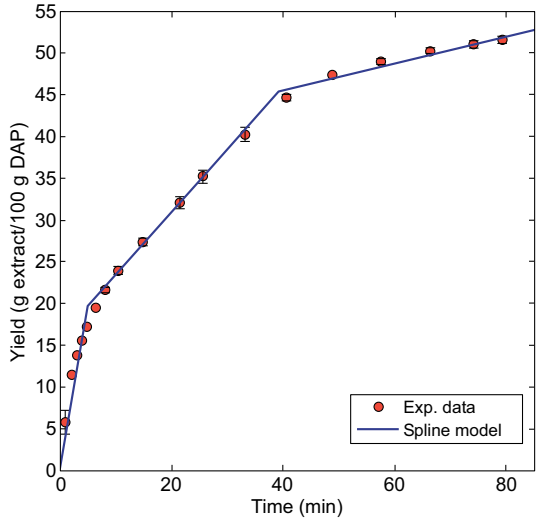


Fig. (4). Extraction curve at 400 bar, 60°C, and 8.6 g CO_2/min.

3.3. Composition of Fatty Acids

The DAP OEY varied due to the effect of temperature and pressure. Nevertheless, these two factors did not affect the fatty acid (FA) profile, showing only small variations in the concentration of FA (Table **3**). Cunha *et al*. [14], proved a similar effect on the *O. distichus* SFE at pressures of 150 to 420 bar and temperatures of 50°C and 60°C, observing a standard deviation less than 1.8% in the content for all FAs. Similarly, Pinto *et al*. [31], reported that under different SFE conditions (pressure: 120 to 420 bar and temperature: 40 and 60°C) of *O. bacaba*, the qualitative profile of the oil was similar, registering variations in the FA content but the predominance of UFA, which varied from 71.9% to 74.0%. The similar effect observed in these two studies was probably due to the similarity in the composition of the FA of the two raw materials, with a more significant predominance of oleic acid in both cases, which could also explain our results. On the other hand, the FA's profile and content in *Virola surinam*ensis oil extracted at 350 bar was varied by the effect of temperature (in the range of 40 to 80°C). In all treatments, the oil was mainly composed of lauric acid (17.3 to 23.5%) and myristic acid (71.7 to 77.6%), increasing and decreasing their concentrations, respectively, with the temperature variation.

The extract obtained in the present study showed three saturated fatty acids (SFAs), two monounsaturated fatty acids (MUFAs), and two polyunsaturated fatty acids (PUFAs). The relative percentages of palmitic, stearic, and arachidic SFAs varied from 21 to 22%, from 1.5 to 1.8%, and from 0.33 to 0.75%, respectively. MUFA, palmitoleic, and oleic contents varied from 0.53 to 0.67% and from 71 to 74%, respectively. PUFAs, linoleic and linolenic varied from 1.5 to 2.2% and from 0.87 to 1.6%. As evident, there is a more significant predominance of oleic and palmitic acid. A higher number of FAs was observed in the DAP extract in our study than in the study by de França *et al*. [5]. They reported the presence of palmitic acid (17.3%), oleic acid (78.7%) and linoleic acid (3.9%) in the oil obtained by SFE-CO_2. Similarly, Jaramillo *et al*. [11], reported the presence of three FAs in the oil extracted with petroleum benzine, myristoleic acid (13.6%), palmitic acid (22.9%), and oleic acid (63.5%). The profile and composition of FA closer to that reported in this study was shown by Jacobo *et al*. [4], applying mechanical extraction at 60°C, the oil obtained by this method in addition to the FA shown in Table **1**, cis-vaccenic (1.3%) and gondoic acids (0.3%). Nevertheless, the oil had a high oleic acid content (74.6%) and palmitic acid (18.4%), which is characteristic of Aguaje pulp. Although small variations in the FA content were recorded (Table **1**), it was possible to observe that the PUFAs extracted at 60°C and 400 bar were in a higher percentage (3.8%).

3.4. Qualitative Profile

Table **4** shows the results of the assays with the five developers (AS, DRG, $Ce(SO_4)_2$, KOH, and $FeCl_3$). The AS and Ce $(SO_4)_2$ developers enabled the detection of phytochemicals. In Fig. (**5**), dark blue stains can be observed with R_f 0.13 and 0.65 for chromatoplate A1, and with R_f 0.11 and 0.55 for chromatoplate A3. This staining is likely to be terpenes after derivatization with AS, as illustrated by Wagner *et al*. [25]. Still, other compounds could also react and emit a similar color because the developer AS is also used in the qualitative identification of compounds such as flavonoids, fatty acids, iridoids, and sugars. With the developer $Ce(SO_4)_2$, it was possible to see two brown spots, as seen in chromatoplates A2 and A3 in Fig. (**5**), which appeared in R_f 0.13 and 0.65 for chromatoplate A2, and in R_f 0.11 and 0.55 for chromatoplate A4. Due to the nature of the sample and the extraction method, it is believed that the compounds that generated these stains are terpenes and/or sterols, but other compounds soluble in sc-CO_2 may also be present. Therefore, it is of great interest to carry out further studies to elucidate which compounds are present in the DAP extract extracted by sc-CO_2 to better explain the functional properties reported in the current scientific literature.

Table 3. Fatty acid composition (%) of DAP extract extracted at different temperatures and pressures.

Fatty acid (%)*	40°C					60°C				
	Pressure (bar)					Pressure (bar)				
	200	**250**	**300**	**350**	**400**	**200**	**250**	**300**	**350**	**400**
C16:0	21±1	22±1	22±1	22±1	22±1	22±1	22±1	22±1	22±1	22±1
C16:1	0.53±0.01	0.63±0.01	0.59±0.01	0.65±0.01	0.65±0.01	0.58±0.01	0.58±0.02	0.56±0.01	0.62±0.01	0.67±0.06
C18:0	1.80±0.1	1.5±0.1	1.7±0.1	1.5±0.1	1.5±0.1	1.6±0.1	1.7±0.1	1.8±0.1	1.6±0.1	1.6±0.1
C18:1	74±1	72±1	73±1	72±1	72±1	73±1	72±1	73±1	72±1	71±1

(Table 3) contd.....

C18:2	1.5±0.1	1.8±0.1	1.7±0.1	1.9±0.1	1.7±0.1	1.7±0.1	1.8±0.1	1.6±0.1	1.8±0.1	2.2±0.4
C18:3	0.87±0.01	1.1±0.1	1.0±0.1	1.2±0.1	1.1±0.1	1.0±0.1	1.1±0.1	0.95±0.03	1.1±0.1	1.6±0.4
C20:0	0.6±0.1	0.43±0.09	0.33±0.01	0.47±0.01	0.75±0.08	0.53±0.01	0.65±0.03	0.53±0.01	0.62±0.02	0.67±0.09
SFA (%)	23±1	24±1	23 ± 1	24±1	24±1	24±1	24±1	24±1	24±1	24±1
MUFA (%)	75±1	73±1	74±1	73±1	73±1	74±1	72±58	74±1	73±1	72±1
PUFA (%)	2.4±0.1	2.9±0.2	2.7±0.2	3.1±0.2	2.8±0.2	2.7±0.2	2.9±0.2	3±1	2.9±0.2	3.8±0.8

Palmitic acid (C16: 0); Palmitoleic acid (C16: 1); Stearic acid (C18: 0); Oleic acid (C18: 1); Linoleic acid (C18: 2); Linolenic acid (C18: 3); Arachidic acid (C20: 0); SFA: Saturated fatty acids; MUFA: Monounsaturated fatty acids; PUFA: Polyunsaturated fatty acids.
* Mean values ± standard deviation (n = 2).

Table 4. Phytochemical profile determined by thin-layer chromatography (TLC) of the DAP extract obtained under different extraction conditions.

Extraction conditions	Anisaldehyde - sulfuric acid	$Ce(SO_4)_2$	KOH	$FeCl_3$	Dragendorff
200 bar-40°C	+	+	-	-	-
250 bar-40°C	+	+	-	-	-
300 bar-40°C	+	+	-	-	-
350 bar-40°C	+	+	-	-	-
400 bar-40°C	+	+	-	-	-
200 bar-60°C	+	+	-	-	-
250 bar-60°C	+	+	-	-	-
300 bar-60°C	+	+	-	-	-
350 bar-60°C	+	+	-	-	-
400 bar-60°C	+	+	-	-	-
(+) Presence, (-) Absence					

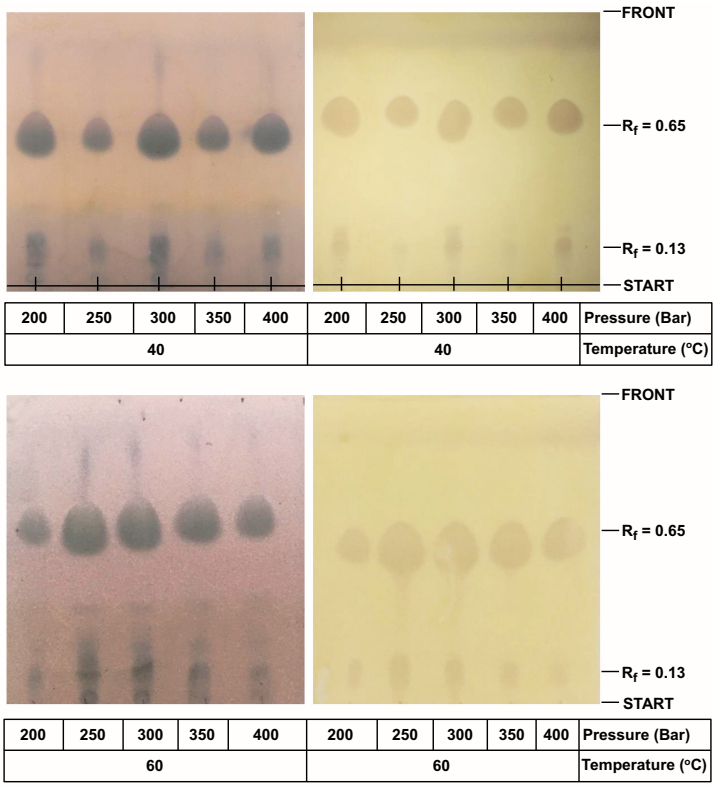


Fig. (5). Identification (A1 and A3 – anisaldehyde developer) and confirmation (A2 and A4 – $Ce(SO_4)_2$ developer) of terpenes by thin-layer chromatography of the DAP extract extracted by SFE at different temperatures and pressures.

Compounds of a terpenic nature have not been reported so far in Aguaje oil extracted by sc-CO_2, but the results observed in this study show evidence of presence of these compounds. Terpenes have already been reported in the leaves of *M.*

flexuosa palm, managing to identify the presence of a diterpene (phytol) and a monoterpene (citronellol), both with essential applications in the cosmetic, food and pharmacologic industries, especially citronellol, as it is a GRAS (generally recognized as safe) substance [36].

CONCLUSION

The pulp of *M. flexuosa* from the collection region is promising for industrial use due to its high lipid content. Supercritical extraction of DAP with CO_2 was performed successfully, and the best extraction conditions were 400 bar and 60°C. Under this condition, it is possible to extract 51.5 g extract/100 g DAP in approximately 79 minutes of the process with a constant flow rate of 8.6 g CO_2/min. The spline model allowed us to characterize the extraction kinetics satisfactorily, observing three extraction periods, CER, FER, and CD, with extraction rates controlled by mass transfer mechanisms by convection, convection-diffusion, and diffusion, respectively. Approximately 87.8% of the extractable DAP at 400 bar and 60°C is obtained in the t_{FER} period (38.99 min). It would be necessary to extend the extraction process for another 40 min to obtain the DAP's total extract; this is not a good practice when considering the process. Therefore, this kinetic point (t_{FER}) is interesting for scale-up studies. The different extraction conditions did not affect the fatty acid profile or the qualitative phytochemical profile, observing the probable presence of compounds from the terpene family. Because of the results obtained, it is necessary to extend the studies for processing on an industrial scale and potential applications in functional foods, drugs, and cosmetics.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals/humans were used for studies that are the basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest, financial or otherwise.

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Artigo 2: **Technical and economic evaluation of supercritical CO_2 extraction of oil from sucupira branca seeds**

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Technical and economic evaluation of supercritical CO_2 extraction of oil from sucupira branca seeds

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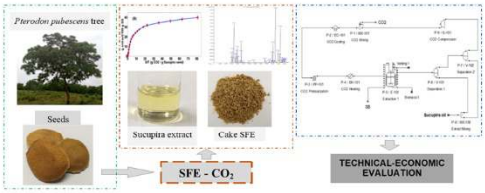
HIGHLIGHTS

- Oil from sucupira branca seeds was obtained by supercritical CO_2.
- 30 MPa and 40 °C of CO_2 was the most suitable condition to obtain 40 wt% oil.
- Phytochemicals such as beta-caryophyllene and alpha-humulene were identified.
- Cost of manufacturing was in the range of 49–124 USD/kg oil in a pilot-scale.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
COM
Cost of manufacturing
Kinetic curves
Supercritical fluid extraction (SFE)

ABSTRACT

Supercritical CO_2 extraction of sucupira branca (SB) seeds was studied under different conditions of pressure (20–40 MPa) and temperature (40 and 60 °C). Operational conditions were assessed on laboratory and pilot scales, and their influences on manufacturing cost (COM) and productivity were discussed. At 40 °C and 30 MPa for 65 min, 40 g oil/100 g SB seeds were obtained. In the economic and technical approaches, a plant with two extractors (2 ×15 L) is more convenient to implement than a plant with one extractor (1 × 30 L), obtaining a COM of 49.21 US$/kg SB oil and productivity of 20,083 kg oil/year. This COM and productivity were reached at the kinetic point where the S/F was 13.5 g CO_2/g SB seeds. In this period, the mass transfer is controlled by diffusion and convection (FER period). The oil obtained under these conditions presented phytochemicals, such as alpha-humulene, beta-caryophyllene, alpha-copaene, (-)-beta-elemene, (*E*)-germacrene D(-)-gamma-elemene, and spathulenol.

1. Introduction

Pterodon emarginatus Vogel is commonly known as sucupira branca (SB) in Brazil, belongs to the Fabaceae family and the genus *Pterodon*, and is distributed in Bolivia and Brazil [1]. This plant belongs to the new group of plant species with great pharmacological potential [2], highlighting the use of its seeds in disease prevention and health promotion. Several investigations have shown the potential use of SB seeds as an

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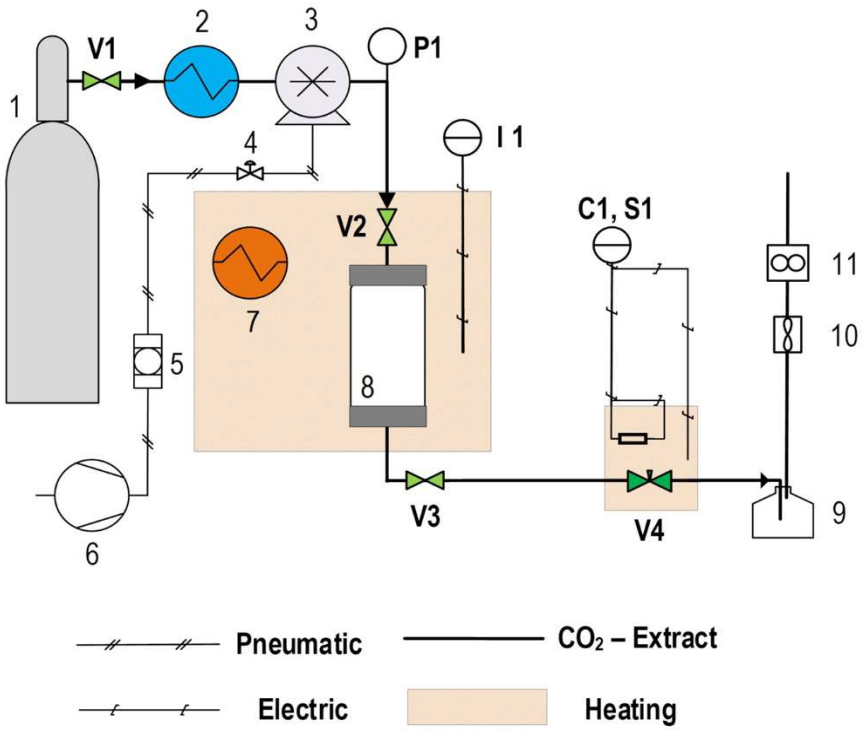

1	CO_2 reservoir	9	Extract collecting vessel
2	Cooling bath	10	Flowmeter
3	Air-driven CO_2 pump	11	Flow totalizer
4	Control (air pressure)	I1	Temperature indicator
5	Air filter	P1	Pressure gauge
6	Air compressor	V1 V2 V3	Blocking valve
7	Heating oven	C1, S1	Controller and sensor
8	Extraction vessel	V4	Micrometering valve

Fig. 1. Spe-ed equipment schematic diagram with modifications in the micrometering valve.

antinociceptive and antibacterial agent for the treatment of edema and in the healing of skin ulcers [3–6].

SB oil is rich in trans-caryophyllene (36%) and alpha-humulene (7%). Both sesquiterpenes have the potential for different pharmaceutical treatments [5,6]. Beta-caryophyllene was administered olfactory as a substitute for the usual drugs given to treat decreased testosterone levels in women with fewer side effects [7]. Skin lesions can be treated topically by supplying beta-caryophyllene [8]. This potential application was evaluated *in vivo* using hydrogel loaded with nanoemulsified beta-caryophyllene [8]. The results showed this product has a high healing power in deep skin wounds, probably because beta-caryophyllene has a potent anti-inflammatory power [8]. Other potential beta-caryophyllene applications are available in the literature [9–11]. Alpha-humulene isolated from the essential oil of *Cordia verbenaceae* can be administered orally for the treatment of inflammatory processes [12]. This same sesquiterpene was also isolated from *Eupatorium odoratum* for *in vivo* and *in vitro* studies. The results demonstrate this sesquiterpene inhibits the proliferation of hepatocellular carcinoma cells [13]. These two sesquiterpenes' potential applications are up-and-coming due to the wide range of bioactive properties and the growing concern about using drugs with natural active ingredients.

SB oil extracted by subcritical CO_2 (20 °C and 12 MPa) showed promising effects for the treatment of *Leishmania amazonensis*, and this effect was attributed to the presence of terpenes [14]. Terpenes are extracted efficiently and selectively with supercritical CO_2 [15,16], which may explain the low yield (14%, mass basis) of oil obtained in a long period (approximately 180 min) of extraction with subcritical CO_2 [14]. Efficient extraction is always desirable for scaling-up purposes and the economic evaluation of the supercritical extraction process [17–20]. The supercritical CO_2 extraction of fruits *Ptedoron* spp. allowed us to obtain oil rich in terpenes with a maximum yield of 21 g oil/100 g raw-material for 80 min at 40 °C and 22 MPa [21]. Supercritical fluid extraction (SFE) of *P. emarginatus* oil at pressures above 12 MPa and the effect of pressure on terpene composition are scarce.

Laboratory-scale studies of the supercritical extraction process are essential for scaling-up the process and assessing the technical and

Table 1
Economic and experimental data used in the simulation for extracting SB oil at the laboratory and pilot scales.

Parameter	Laboratory scale (2 ×1 L)	Pilot-scale 1 (2 ×15 L)	Pilot-scale 2 (1 ×30 L)	Dimension
Fixed capital investment (FCI)				
Plant[a]	31,343.00	186,362.00	208,043.00	US$
Annual depreciation	10	10	10	%
Annual maintenance rate	6	6	6	%
Annual inflation rate	4	4	4	%
Project lifetime	25	25	25	Years
Annual working time	2640	5280	5280	h/year
Daily working time	8	16	16	h/day
Project financing	80	80	80	%
Loan period	10	10	10	Years
Loan interest	9	9	9	%
Cost of raw material (CRM)				
SB fresh seeds	9.00	6.00	6.00	US$/kg
Commercial CO_2 (99% purity)	3.00	2.00	2.00	US$/kg
Cost of operational labor (COL)				
Wage (With benefits and administration)	8.00	8.00	8.00	US$/h. worker
Worker	2	3	3	Worker/ shift
Daily shift	1	2	2	Shift
Annual total wage	42,240.00	126,720.00	126,720.00	US$/year
Cost of utilities (CUT)				
Water (for cleaning)	1.00	1.00	1.00	US$/$m^3$
Electricity	0.25	0.25	0.25	US$/kW.h
Estimation of the selling price				
SB oil[b]	166.27	166.27	166.27	US$/kg

[a] Estimated according to the power-law equation [22].
[b] https://www.mundodosoleos.com/ (access date: 13-06-2020).

economic feasibility. For this purpose, scaling-up criteria of a constant S/F ratio or extraction solvent flow rate can be adopted [17,22], and using a constant S/F ratio implies that the extraction time and the solvent flow rate must be adjusted appropriately for the pilot-scale process to be technically feasible [23]. An S/F value of 13 was used to scale up the grapeseed oil extraction process, resulting in a technically viable and economically feasible project [17]. With this S/F value, 90% of oil could be extracted. Otherwise, SFE of the remaining 10% of oil is not economically viable because the extraction of this last fraction is controlled by the phenomenon of diffusion. Therefore, it increases the processing time, which would increase production costs and decrease productivity [17]. The scaling-up of a SFE process, taking into account the mass transfer mechanisms, is important. For industrial purposes and considering that the dominant mass transfer mechanism is given by convection, a constant S/F ratio is a rapid and simple strategy procedure for supercritical technology development to industrial scale [18,23].

The increase in the S/F as a consequence of the increase in the extraction time increases the yield. However, depending on each specific project, it can increase the manufacturing cost (COM) and decrease the productivity of bioactive extracts [20,22,24]. The kinetics of experimental extraction at laboratory scale provide relevant information about SFE process. Even though several phenomenological models are displayed to represent the SFE process [25], the spline empirical model is simple and practical to be applied as it represents the extraction periods of diffusion and convection through the changes in the slopes of the kinetic curves [26]. This model allows correlating the global yield with the extraction time. With this, the right S/F ratio is calculated to have a higher yield with a shorter extraction time. Generally, the raw materials subjected to grinding present solute easily accessible for the solvent, located in the superficial part of the particles and the broken cells; their extraction occurs in the first stages of the process and is controlled by convection [26,27]. Therefore, the use of a constant S/F ratio for scale-up purposes is suitable either by experimental [23] or process simulation [26]. Furthermore, the cost of manufacturing can be calculated using the yield of each extraction cycle determined by the spline model [26]. The extraction temperature and pressure are often studied to improve the solvation power of supercritical CO_2, seeking to increase the extraction yield while maintaining a low S/F and extraction time. On the industrial scale, the decrease in particle size positively affects the extraction cost, increasing the contact surface area between the solvent and the particles present in the extraction bed. Particle sizes larger than 1 mm are recommended, as smaller particles can cause problems in channeling the bed due to solvent flow [28].

Therefore, the current study aimed to evaluate the supercritical CO_2 extraction of oil from *P. emarginatus* seeds at pressures higher than those reported in the literature (20, 30, and 40 MPa). The objective was to determine the best process conditions with low cost of manufacturing (COM) and high oil productivity. The quality of the oil in terms of the composition of bioactive compounds was also investigated.

Information on the SFE of SB and its composition is very limited in the literature. According to our review, SB oil extraction was carried out by conventional techniques [5,14] and by subcritical extraction [14]. The results of these studies show extraction yields lower than those obtained in our study. SB oil is commercially available [29] and obtained under different conventional extraction techniques. With our study, we verified that the extraction of SB oil is more efficient with supercritical CO_2. However, the effect of the application of this technology on the production cost was unknown. Therefore, in the second stage of the present study, which shows the analysis of the production cost, we verify that SB oil production is economically viable using pilot plants. Finally, phytochemical composition of SB oil is promising due to the considerable number of compounds identified, highlighting the concentrations of alpha-humulene and beta-caryophyllene, both of which are of high commercial value.

2. Material and methods

2.1. Sample

SB seeds were collected from the city of *Pontal do Araguaia* of *Mato Grosso* State (Brazil). They were manually selected and stored at − 18 °C for transportation to the laboratory (LASEFI/FEA/UNICAMP). The seeds were ground in a knife mill (Marconi, MA 340, São Paulo, Brazil) for extraction. The average particle diameter was 0.87 ± 0.12 mm, determined according to the methodology of the American National Standard Institute [30].

2.2. Extraction equipment

The extractions were performed in SFE-Spe-ed equipment (Applied Separations, model 7071, Allentown, USA) with a homemade modification in the heating system of the micrometering valve (Fig. 1, item V4). The 500-Watt home heating system is composed of a temperature controller (Autonics, REF TK^4S–^{14}SN, Brazil), a Pt100 temperature sensor, and a reservoir containing distilled water with natural circulation maintained at approximately 55 °C where the body of the micrometering valve was submerged. The modified equipment's operational procedure is well described in the research group's previously published work [22].

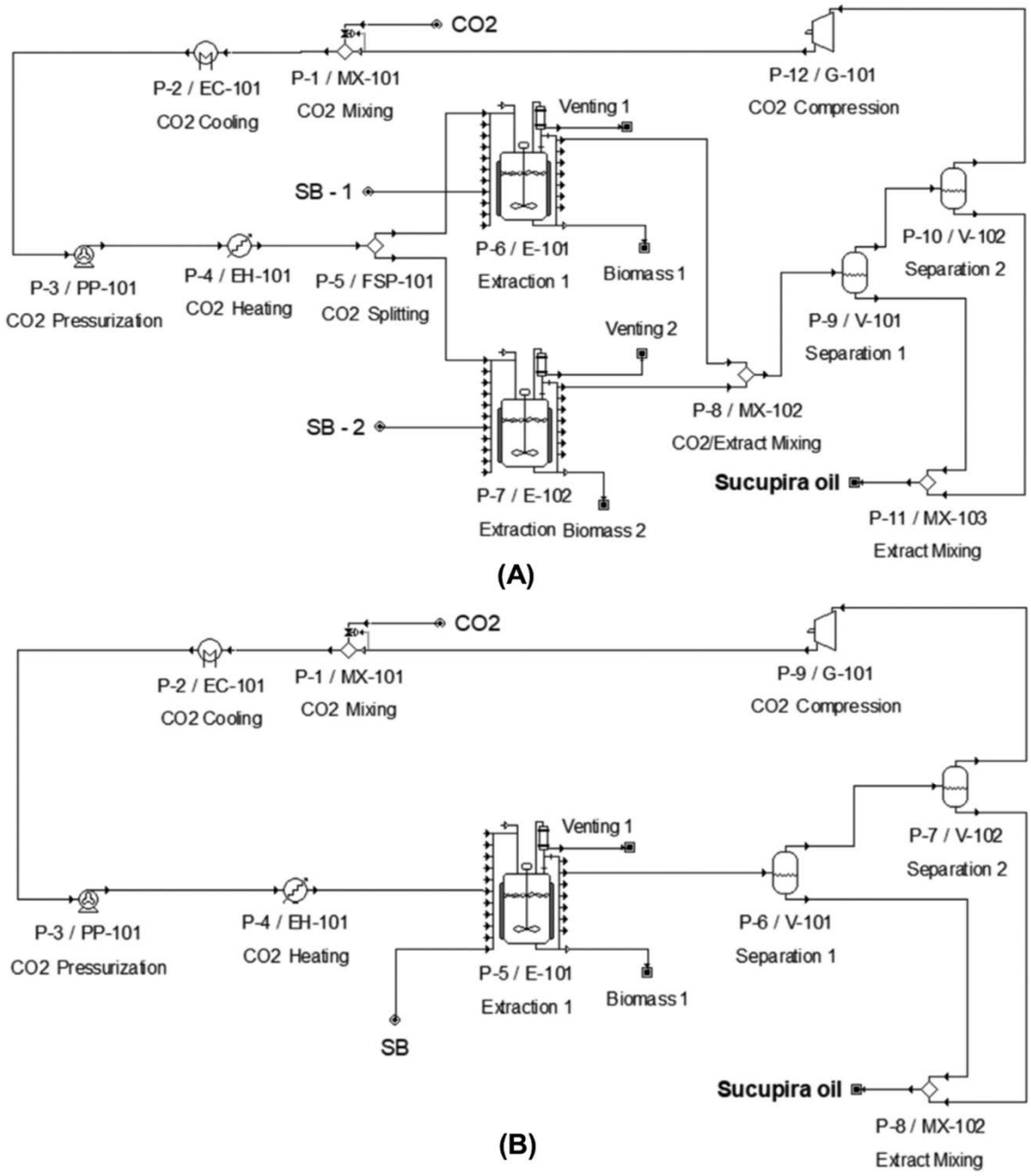

Fig. 2. Flowsheet of the 2 × 15 L (A) and 1 × 30 L (B) plants applied in the simulation of manufacturing SB oil on pilot scales.

2.3. Supercritical CO_2 extraction of SB oil

Initially, the pressure and temperature effect on the extraction yield of SB oil was evaluated at 20, 30 and 40 MPa at 40 and 60 °C. The extractions were performed by loading a 5 mL extraction vessel with 3.6 g of ground SB seeds. The extraction assays were performed with CO_2 (White Martins, 99% purity, Campinas, Brazil) at a constant flow rate (4.5 g/min) for an extraction time of 11 min, therefore reaching a solvent-to-feed mass ratio (S/F) of approximately 12 g CO_2/g SB seeds. These S/F ratios and extraction times were selected based on the extraction assays carried out with *Pterodon* spp. fruits; during this period, extraction occurs predominantly by convection, according to the values of the mass transfer coefficients obtained with the Sovová model [21]. The best temperature and pressure condition that allows the highest overall extraction yield was determined from this first evaluation.

The best pressure and temperature conditions were used to perform a complete SB oil extraction in the next stage. During the extraction, extract samples were collected at different time intervals to determine the extraction kinetics. For the extraction, 3.6 g of SB seeds were loaded into a 5 mL extraction vessel. A CO_2 flow rate of 4.5 g/min was used, and the total extraction time was 65 min, with a final S/F ratio of approximately 81 g CO_2/g of SB seeds.

Before starting the dynamic extraction, a 5 min static extraction was performed in all extraction assays. The static extraction consisted of keeping the extraction bed with CO_2 flow after pressurization and temperature conditioning.

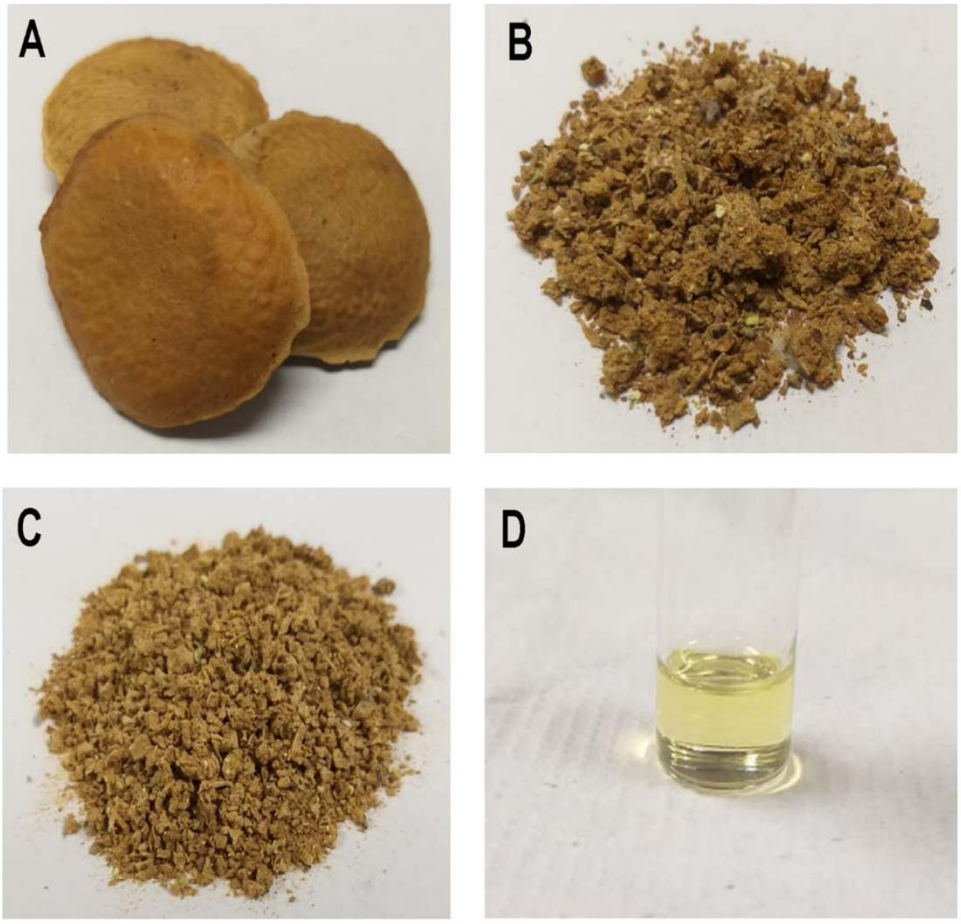

Fig. 3. Photos of SB integer seeds (A), ground seeds before extraction (B), ground seeds after extraction (C), and SB oil (D).

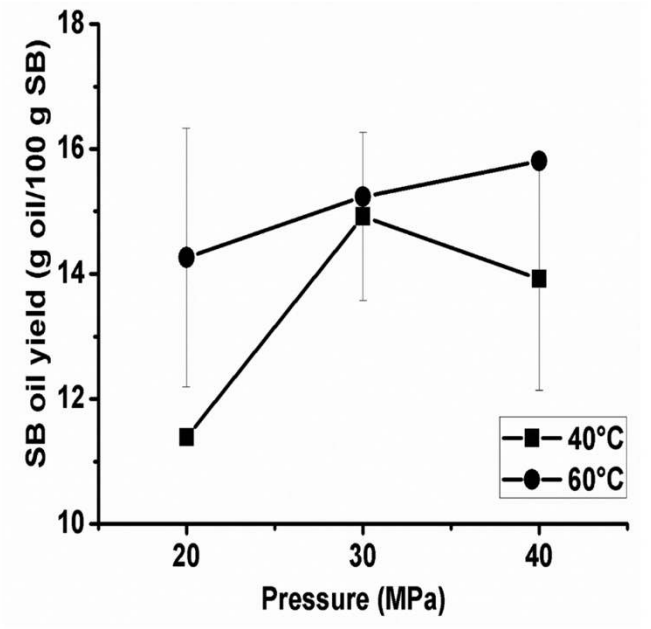

Fig. 4. SB oil extraction isotherms (mean ± standard deviation (error bars)) for an S/F ratio of 13.5 g CO_2/g SB seeds and 11 min of supercritical extraction.

2.4. Spline model

The spline model was used to fit the kinetic extraction data; this model was previously described by Meireles [26], who described that the global extraction curve typically presents three different periods with three different extraction rates. Initially, a period of constant extraction rate (CER) is found, in which the oil contained on the surface of the particles is recovered mainly by convection. A reduction in the rate characterizes the following period, named falling extraction (FER), in which the extraction is carried out by convection and diffusion. Finally, a period controlled by diffusion (DC) is found. The spline model is shown in Eqs. (1)–(3).

$$m_{Ext} = a_1 t;\ t < t_{CER} \tag{1}$$

$$m_{Ext} = a_1 t_{CER} + a_2 (t - t_{CER});\ t_{CER} \leq t < t_{FER} \tag{2}$$

$$m_{Ext} = a_1 t_{CER} + a_2 (t_{FER} - t_{CER}) + a_3 (t - t_{FER});\ t_{FER} \leq t \tag{3}$$

Where m_{Ext} is the extraction yield (g oil/100 g raw material); a_1, a_2, and a_3 are the slope coefficients (first-order terms) of CER, FER, and DC straight lines, respectively (min^{-1}); t_{CER} is the time interval of the CER period (min); and t_{FER} is the end of the FER period (min).

The fit quality of the experimental data to the spline model was evaluated considering the objective function defined as the absolute average relative deviation (AARD) referred to the yield expressed by Eq. (4) [31]:

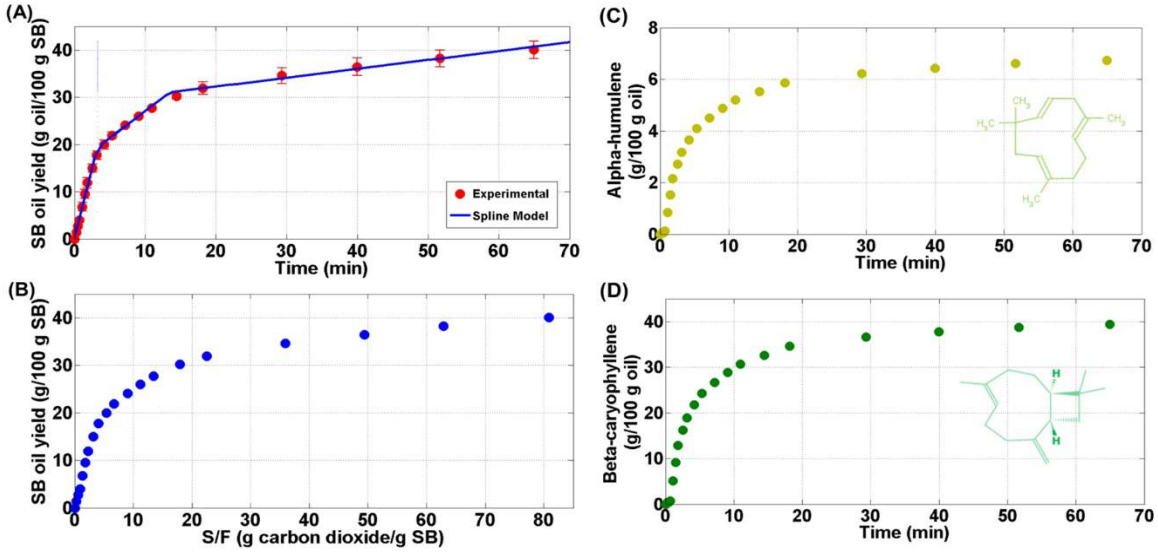

Fig. 5. Extraction kinetics of SB oil (A and B), alpha-humulene (C), and beta-caryophyllene (D) using CO_2 at 40 °C and 30 MPa.

$$\text{AARD}(\%) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}}\right| \quad (4)$$

where AARD is the average absolute relative deviation (%), n is the number of data, $x_{i,exp}$ and $x_{i,cal}$ refer to the experimental and calculated yields for data i, respectively.

2.5. Chromatographic analysis

The composition of SB oil was determined using a gas chromatograph (Agilent, 5975 C, USA) coupled with a quadrupole-type mass spectrometer with the following characteristics: a source of ionization - electron impact (70 eV), scan mode of 0.5 s/scan, a mass range of 30–500 Daltons (u), and transfer line of 280 °C. An HP-5MS column composed of 5% diphenyl and 95% dimethyl polysiloxane (30 m × 0.25 mm, 0.25 μm) was used. The SB oil was diluted with chromatographic *n*-hexane and injected into the column (1.0 μL) with a split mass ratio of 1:100. The carrier gas was helium (99.9999% purity) at 1.0 mL/min. The injector temperature was 220 °C. The column was heated from 60 °C to 240 °C at 3 °C/min, 280–10 °C/min and maintained at 280 °C for 5 min. A chromatographic run time of 69 min was set for each sample. The NIST11 mass spectrum database was used to identify the compounds detected in the investigated samples [32].

The contents of beta-caryophyllene and alpha-humulene in SB SFE extract obtained under the best extraction conditions were investigated. The quantification of these two terpenes was carried out at different periods of the extraction process to describe the two compounds' extraction kinetics. The analysis was carried out following the methodology developed in previously published works [33,34]. The samples obtained at different extraction times were diluted with 25 mL of ethyl acetate (99.5% purity, Dinamica, Diadema, Brazil). The diluted extracts were analyzed by gas chromatography with flame ionization (GC-FID) (SHIMADZU, CG 17-A, Kyoto, Japan) with a fused silica capillary column ZB-5 (30 m × 0.25 mm, 0.25 μm, Phenomenex, Torrance, USA). The carrier gas was helium (99.9% purity, White Martins, Brazil) at a total flow rate of 26 mL/min and a column flow rate of 1.11 mL/min. An injection volume of 1 μL and a split mass ratio of 1:20 were used. The injector and detector temperatures were 220 °C and 240 °C, respectively, and the initial temperature of the column was 60 °C. Based on a defined program, the column was heated from 60 °C to 240 °C at 3 °C/min and then held for 2 min. A chromatographic run time of 62 min was set for each sample. Quantification of these two compounds in the samples was performed using the retention time and calibration curves for standards of beta-caryophyllene (Merck, Sigma-Aldrich, purity ≥ 80%, USA) and alpha-humulene (Merck, Sigma-Aldrich, purity ≥ 90%, USA).

2.6. Economic evaluation

The processing of supercritical CO_2 extraction of SB seeds was evaluated from an economic viewpoint in different operational scenarios, considering that the observed experimental behavior remains similar between the different scales evaluated. The purpose is to present an initial behavior of a range of costs related to obtaining SB oil by supercritical technology, discussing the main influences of the relative costs.

The apparent density of the extractive bed of 700 kg/m^3 used in the experimental assays was considered for the economic evaluation. SuperPro Designer 9.0® software (Intelligen Inc., Scotch Plains, NJ, USA) was used to simulate the process and obtain the economic parameters. The study was divided into two stages: 1) In the first stage, the results of the extraction kinetics under the best extraction conditions (30 MPa and 40 °C) (Fig. 5A) and the data described in Table 1 were used for the laboratory-scale simulation (1.4 kg of SB seeds for each batch; plant of 2 × 1 L). The manufacturing cost (COM, in US$/kg of oil) and productivity (kg of oil/year) were the responses taken into account; 2) In the second stage, the same responses were evaluated on a pilot scale where the increase in capacity was 15 times (21 kg of SB seeds for each batch), considering extraction plants of 2 × 15 L (two extraction vessels of 15 L each operating in semicontinuous mode disposed of in a parallel configuration; Figs. 2A) and 1 × 30 L (one extraction vessel of 30 L; Fig. 2B). For both stages, an additional 20% of the investment cost for additional equipment (balances, freezers, *etc.*), annual depreciation of 10% and inflation of 4%, and an equipment maintenance cost of 6% were considered [35]. It is essential to note that the supercritical extraction of bioactive compounds on a pilot scale considering relatively low volumes (30 L) is relevant. This claim can be justified because SB seed production is seasonal [3]. The CO_2 was recycled in the compress using a compression system (Fig. 2).

The COM and the percentage contribution of the itemized costs (fixed capital investment – FCI; the cost of raw materials – CRM; the cost of operational labor – COL; cost of utilities - CUT) were evaluated using the typical default models of the SuperPro simulator. The economic return scenarios considered the gross margin (GM), the return on

Table 2a
Chromatographic analysis of SB seed oil extracted at 30 MPa and 40 °C.

Peak	Rt (min)	CAS[a]	Name	Area percent (%)	Quality[b]
1	20.014	003856-25-5	alpha-copaene	1.42	99
2	20.608	013744-15-5	beta-cubebene	0.76	97
3	20.762	000515-13-9	(-)-beta-elemene	2.22	91
4	21.902	000087-44-5	beta-caryophyllene	10.71	99
5	23.124	006753-98-6	alpha-humulene	1.21	97
6	23.38	025246-27-9	alloaromadendrene	0.58	99
7	24.252	023986-74-5	(*E*)-germacrene D	2.02	96
8	24.489	000473-13-2	alpha-selinene	0.17	83
9	24.881	029873-99-2	(-)-gamma-elemene	2.72	91
10	25.184	000515-13-9	(-)-beta-elemene	0.96	90
11	25.635	–	NI	0.13	–
12	26.953	001139-30-6	beta-caryophyllene oxide	0.21	70
13	27.487	–	NI	0.18	–
14	28.146	006750-60-3	spathulenol	5.39	76
15	28.798	1000156-11-0	diepicedrene-1-oxide	0.13	95
16	28.911	000577-27-5	ledol	0.12	99
17	29.125	019888-34-7	humulene oxide II	0.24	74
18	30.288	–	NI	0.18	–
19	33.861	–	NI	0.14	–
20	35.179	000489-40-7	alpha-gurjunene	0.29	91
21	38.811	000295-65-8	cyclohexadecane	0.4	98
22	40.479	–	NI	0.17	–
23	44.201	017367-08-7	ethanol, 2-(9,12-octadecadienyloxy)-, (*Z,Z*)-	0.10	94
24	45.186	007206-21-5	5-Octadecene, (*E*)-	0.10	98
25	48.314	–	NI	0.71	–
26	49.352	–	NI	0.25	–
27	49.75	–	NI	0.3	–
28	51.584	–	NI	0.14	–
29	52.249	–	NI	0.73	–
30	53.721	–	NI	0.21	–
31	53.923	–	NI	0.31	–
32	54.522	000472-33-3	vinhaticol	3.54	83
33	55.282	–	NI	5.17	–
34	55.418	005939-62-8	cupressene	0.19	89
35	55.911	–	NI	0.26	–
36	56.38	–	NI	0.85	–
37	57.324	–	NI	37.19	–
38	57.602	010147-56-5	D-Homoandrostan-17a-one,(5.alpha)-	0.18	70
39–55	58–66.541	–	NI	19.4	–

Rt: retention time
NI: Not identified
Area percent (%): Percentage of the normalized area which indicates the relative distribution of compounds in the sample
[a] CAS registry numbers
[b] Research index in the database that reflects the similarity of the mass spectrum obtained with that recorded in the NIST11. L library. Quality indices ≥ 70

investment (ROI), and the payback time.

2.7. Statistical analysis

A two-way analysis of variance (ANOVA) was performed to determine the effect of factors (pressure and temperature) on extraction yield, and the *Bonferroni* test determined significant differences. Both analyses were performed at a significance level of 0.05 using Origin software version 8.1 (OriginLab Corporation, Northampton, MA, USA).

3. Results and discussion

3.1. SB oil extraction

The SB tree produces a large number of seeds between June and July. The seeds are rounded (Fig. 3A) with a porous and fibrous woody internal structure containing an oily substance [3], which could explain the particle agglomeration after grinding (Fig. 3B). The seeds ground before and after supercritical CO_2 extraction are shown in Figs. 3B and 3C, respectively. The SB oil extracted by supercritical CO_2 showed a yellowish crystalline aspect (Fig. 3D).

The pressure and temperature effects on the SB extraction yield are shown in Fig. 4, in which the extractions were performed for 11 min and an S/F ratio of 12 g CO_2/g SB seeds. The yields were superior to the results reported by Favareto et al. [21], in which the extraction of oil from fruits of *Pterodon* spp. for the same extraction time at 22 MPa and 40 °C was reported (approximately 7.5 g oil/100 g raw material). Additionally, the SB extraction yields were superior to the yield (approximately 4.4 g oil/100 g raw-material) from *Pterodon pubescens* benth (synonymous *Pterodon emarginatus* Vogel) using subcritical CO_2 extraction (20 °C and 12 MPa) for 50 min [14]. Similarly, our results are superior to the yields obtained by hydrodistillation (3.9 g of oil/100 g of raw material) [5], maceration with ethanol, and turbo extraction with ethanol [14]. The highest extraction yield found in this work is most likely associated with the edaphoclimatic conditions of cultivation and because supercritical technology is more efficient in the extraction of volatile oils [36–39].

The temperature variation from 40 to 60 °C and the interaction between temperature and pressure had no significant effect (p-value > 0.05) on the extraction yield. This behavior was different when the pressure ranged from 20 to 40 MPa (p-value < 0.01). The *Bonferroni* test showed that the mean SB SFE yields were significantly different when the pressure ranged from 20 to 30 MPa and from 20 to 40 MPa, while the average yields obtained at 30 and 40 MPa were not significantly different, considering a significance level of 0.05. In the 60 °C isotherms, the oil yield increased by 6.6% (from 14.3 to 15.2 g/100 g SB seeds) and 10.5% (from 14.3 to 15.8 g/100 g SB seeds) when the pressure was increased from 20 to 30 MPa and 20–40 MPa, respectively. The increase in the yield can be explained by the increase in the solvation power of CO_2 when the pressure increases at a constant temperature [39,40]. Otherwise, the behavior was different in the 40 °C isotherms. The yield increased when the pressure increased from 20 to 30 MPa but remained practically constant from 30 to 40 MPa. This phenomenon is described elsewhere as retrogradation of solubility [41].

ANOVA and the *Bonferroni* test showed that temperature did not significantly influence (p-value > 0.05) the extraction yield, which may have occurred due to the standard deviation of the experimental data (Fig. 4). Considering the average values of the overall extraction yield when the temperature varied from 40° to 60°C, they increased 25.6% (from 11.4 to 14.3 g oil/100 g SB seeds) and 13.5% (from 13.9 to 15.8 g oil/100 g SB seeds) for 20 and 40 MPa, respectively. A smaller increase was observed at 30 MPa, where it was 2.1% (from 14.9 to 15.2 g oil/100 g SB seeds). This behavior can be explained by the variation in the solute vapor pressure, which depends on the extraction process's temperature [41–43]. Although the average yield at 40 MPa and 60 °C was higher than all other extraction conditions, this was only 5.9% higher

Table 2b
Chromatographic analysis of SB seed oil extracted at 20 MPa and 40 °C.

Peak	TR	CAS[a]	Name	Area percent (%)	Quality[b]
1	20.02	003856-25-5	alpha-copaene	1.56	96
2	20.614	013744-15-5	beta-cubebene	0.84	97
3	20.774	000515-13-9	(-)-beta-elemene	2.3	91
4	21.931	000087-44-5	beta-caryophyllene	11.62	99
5	23.136	006753-98-6	alpha-humulene	1.33	97
6	23.385	025246-27-9	alloaromadendrene	0.62	99
7	24.258	023986-74-5	(*E*)-germacrene D	1.7	96
8	24.893	029873-99-2	(-)-gamma-elemene	2.59	91
9	25.196	010219-75-7	eremophilene	0.83	95
10	26.958	083085-83-0	1,Z-5,E-7-Dodecatriene	0.26	83
11	27.487	–	NI	0.19	–
12	28.175	–	NI	4.88	–
13	28.235	001139-30-6	beta-caryophyllene oxide	1.43	94
14	29.131	019888-34-7	humulene oxide II	0.26	74
15	30.288	–	NI	0.21	–
16	35.179	000483-75-0	alpha-amorphene	0.23	89
17	38.817	000295-65-8	cyclohexadecane	0.39	99
18	48.32	–	NI	0.69	–
19	49.75	–	NI	0.27	–
20	53.249	–	NI	0.52	–
21	53.928	–	NI	0.22	–
22	54.528	000472-33-3	vinhaticol	2.95	83
23	55.305	–	NI	5.53	–
24	55.43	020070-61-5	kaur-16-ene, (8β,13β)-	0.18	91
25	56.406	–	NI	0.71	–
26	57.365	–	NI	38.84	–
27–39	59.341–65.752	–	NI	18.43	–

TR: Compound retention time in column in minutes
NI: Not identified
Area percent (%): Percentage of the normalized area which indicates the relative distribution of compounds in the sample
[a] CAS registry numbers
[b] Research index in the database that reflects the similarity of the mass spectrum obtained with that registered in the NIST11. L library. Quality indices ≥ 70

than the yield at 30 MPa and 40 °C. Based on that, lower temperatures and pressures are desirable in the extraction of bioactive compounds, and taking into account the standard deviation, the extraction conditions of 30 MPa and 40 °C were selected as the best conditions for the kinetic study.

3.2. Kinetics and spline model

The SB seed oil extraction kinetics at 30 MPa and 40 °C were adjusted to the spline model [26], as shown in Fig. 5. The ARRD value of 4.7% showed that the spline model was adequately adjusted to the experimental data, as recommended in the literature [31]. The extractions were well described by the three straight lines of the model: CER, FER, and DC. The parameters obtained from the spline model were the mass transfer rate for the CER period (m_{CER}) of 5.91 g oil/(100 g SB. min), the mass transfer rate for the FER period (m_{FER}) of 1.14 g oil/(100 g SB.min), the mass transfer rate for the DC period (m_{DC}) of 0.17 g oil/(100 g SB.min), t_{CER} of 3.29 min, and t_{FER} of 13.51 min

The t_{CER} and t_{FER} obtained in this work were lower than in the extraction kinetics at 22 MPa at the same temperature for *Pterodon* spp. fruits [21]. These findings are interesting for process scaling purposes because shorter times with higher yields are desirable for the process's economy and higher productivity. At the end of these two periods (CER and FER), it was possible to extract 48.5% (19.44 g/100 g SB seeds) and 77.6% (31.09 g/100 g SB seeds) of the extractable oil from the SB seeds, respectively. The mass of SB oil obtained in the t_{FER} (3.29 min) was close to 21 g oil/100 g raw material reported by Favareto et al. [21], after 80 min of *Pterodon* spp. extraction. This result can be explained by the high mass transfer rate observed in this period ($m_{CER} = 5.91$ g oil/(100 g SB.min)). These three periods were also observed in the extraction of rice oil, reaching an m_{CER} of 3.98 g oil/(100 g.min) [44], which was lower than our result.

The yields obtained in the CER and FER periods are promising for the extraction process on larger scales due to the high mass transfer rates. Initially, in the CER period (3.29 min), the easily accessible extract is recovered, this stage of the extraction is controlled by a convection mass transfer mechanism [26]. Near the end of this period, the mass transfer rate decreases because it is controlled by diffusion and convection, typical of the FER period [26]. These two extraction periods were considered for process simulation and economic evaluation, using a constant S/F ratio of 13.5 g CO_2/g SB seeds as a scaling-up criterion, according to the experience reported in supercritical peach seed extraction [18] and the production of quercetin-rich powdered extracts [45].

3.3. Composition of SB oil

The composition of SB oil extracted at 40 °C and 20 MPa, which is a condition close (40 °C and 22 MPa) to that reported in the extraction of oil from *Pterodon* spp. [21], was compared with the oil obtained under the best conditions (40 °C and 30 MPa) found in this work. More compounds were detected and identified in the extraction at 30 MPa (Table 2a) than at 20 MPa (Table 2b). Fifty-five compounds were detected in the SB oil obtained at 30 MPa, of which twenty-two were identified. At 20 MPa thirty-nine compounds were detected, of which sixteen compounds were identified. Twelve compounds were identified in the SB oil obtained in both extraction conditions: alpha-copaene, beta-cubebene, (-)-beta-elemene, beta-caryophyllene, alpha-humulene, alloaromadendrene, (*E*)-germacrene D, (-)-gamma-elemene, beta-caryophyllene oxide, humulene oxide II, and cyclohexadecane. This finding confirms that the SB oil obtained in the best extraction condition (30 MPa and 40 °C) observed in our study has a higher quality bioactive compound composition. Beta-caryophyllene and alpha-humulene are frequently reported in SB oil, with beta-caryophyllene being the most considerable constituent [2,5,6]. Indeed, these two compounds were found in the oil of the two extraction conditions evaluated. In the kinetic study of SB oil extraction, these two compounds were evaluated over time (Fig. 5). Concentrations of 6.74 g

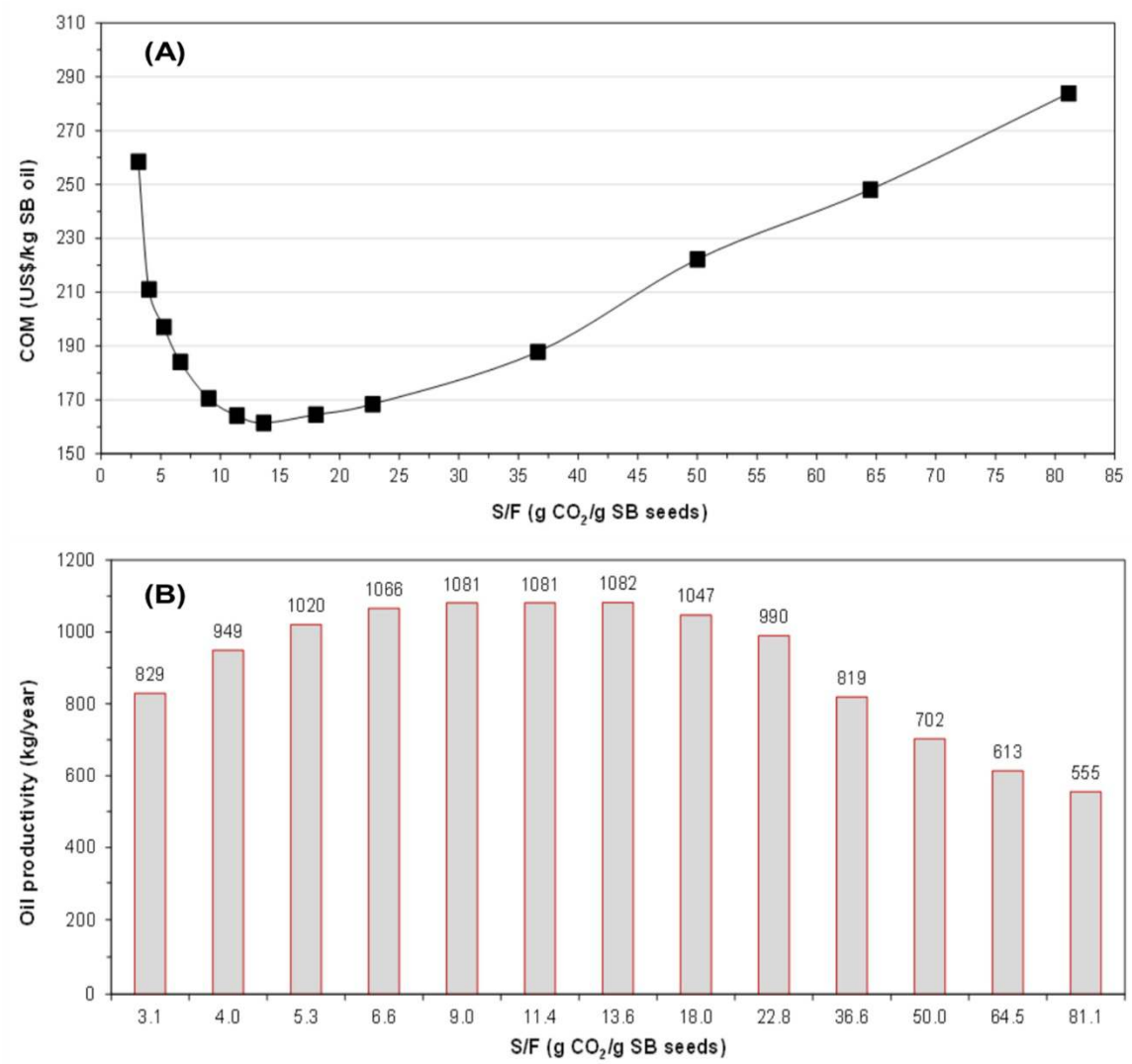

Fig. 6. COM and productivity of SB seed oil obtained by supercritical CO_2 in a 2 × 1 L plant at 30 MPa and 40 °C.

Table 3
Parameters of profitability for obtaining SB oil in different scenarios.

Plant	Scenario	COM (US $/kg oil)	GM (%)	ROI (%)	Payback time (year)	NPV* (US $)	Operating cost (US$/year)	Gross Profit (US $/year)	Main revenue (US$/year)
2 × 1 L	1 - Normal	161.53	2.85	2.90	34.51	-3000	175,000	5000	180,000
2 × 15 L	2 - Normal	49.21	70.40	306.34	0.33	29,064,000	988,000	2,351,000	3,339,000
1 × 30 L	3 - Normal	61.90	62.77	166.64	0.60	24,659,000	1,190,000	2,007,000	3,197,000
2 × 15 L	4 - Double cost plant	54.59	67.17	134.56	0.74	27,507,000	1,096,000	2,243,000	3,339,000
1 × 30 L	5 - Double cost plant	68.51	58.80	83.04	1.20	22,825,000	1,317,000	1,880,000	3,197,000
2 × 15 L	6 - Double cost of raw materials	81.36	51.07	199.34	0.50	20,943,000	1,634,000	1,705,000	3,339,000
1 × 30 L	7 - Double cost of raw materials	100.21	39.73	97.35	1.03	15,393,000	1,927,000	1,270,000	3,197,000
2 × 15 L	8 - Double wage and double workers	67.99	59.11	241.05	0.41	24,320,000	1,365,000	1974,000	3,339,000
1 × 30 L	8 - Double wage and double workers	79.79	52.01	132.89	0.75	20,331,000	1,534,000	1663,000	3,197,000
2 × 15 L	10 – All the 4, 6 and 8 scenarios together	105.51	36.54	67.55	1.48	14,643,000	2,119,000	1220,000	3,339,000
1 × 30 L	11 – All the 4, 6 and 8 scenarios together	124.72	24.99	33.14	3.02	9,232,000	2,398,000	799,000	3,197,000

COM: manufacturing cost; NA: Not applicable; GM: gross margin; ROI: return over investment; NPV* : net present value at 7% interest.

Table 4
COM, productivity, FCI, CRM, COL, and CUT for obtaining SB oil in 2 × 1 L, 2 × 15 L, and 1 × 30 L in 11 min (S/F ratio of 13.5) of extraction at 30 MPa and 40 °C.

Plant	Pre-conditions for each vessel	Post-conditions for each vessel	Productivity (kg oil/year)	COM (US $/kg oil)	FCI (%)	CRM (%)	COL (%)	CUT (%)
2 × 1 L	Loading (5 min), pressurization (5 min), and static time (5 min)	Depressurization (5 min) and unloading (5 min)	1082	161.53	9.18	54.33	33.06	3.43
2 × 15 L	Loading (10 min), pressurization (15 min), and static time (10 min)	Depressurization (10 min) and unloading (10 min)	20,083	49.21	7.81	65.32	12.72	14.15
1 × 30 L	Loading (15 min), pressurization (25 min), and static time (15 min)	Depressurization (15 min) and unloading (15 min)	19,227	61.90	10.68	61.89	9.64	17.79

COM: Manufacturing cost; FCI: Fixed capital investment; CRM: Cost of raw material; COL: Cost of operational labor; CUT: Cost of utilities.

alpha-humulene/100 g SB oil and 39.4 g beta-caryophyllene/100 g SB oil were reached at the end of the extraction (65 min and S/F ratio of 81 g CO_2/SB seeds). These results are close to those reported by Dutra et al. [5] and Dutra et al. [6] for SB oil, in which they found mass concentrations of 36% beta-caryophyllene and 6.8% alpha-humulene, respectively. From the kinetic study, the concentration of these two compounds in the oil at 11 min extraction (extraction time used in the process simulation and economic evaluation) was 5.9 g alpha-humulene/100 g SB oil and 34.9 g beta-caryophyllene/100 g SB oil, which is approximately 88–89% of the total yield for the two compounds found at the end of extraction time.

SB seed oil is a promissory source of beta-caryophyllene and alpha-humulene. These sesquiterpenes have bioactive properties, such as antiulcerogenic and anti-inflammatory activities [6,12], enabling the development of natural drugs with different applications. Recently, beta-caryophyllene has shown a positive effect on the increase of testosterone in women with loss of libido and can substitute for the usual drugs [7]. Hydrogels loaded with nanoemulsified beta-caryophyllene effectively treated skin lesions [8]. Other potential applications of beta-caryophyllene are cardioprotective [9], in the treatment of periodontal disease [10], dental cavity [11], and antiarthritic [46]. Alpha-humulene inhibited the proliferation of hepatocellular carcinoma cells [13], as a natural insecticide [47], and as an oral anti-inflammatory agent [12].

3.4. Economic evaluation

The economic analysis of SB oil production was carried out, taking into account the current commercial value of US$ 166.27 per liter of SB oil [29]. The results of the economic simulation of the laboratory-scale extraction process (2 × 1 L), considering the extraction kinetics data (Figs. 5A and 5B) under the best conditions (30 MPa and 40 °C), are shown in Fig. 6A and B. There is a decrease in COM as the S/F ratio increases from 1 to approximately 13.5 g CO_2/g SB. From this S/F ratio (13.5 g CO_2/g SB), the COM starts to increase due to reduced productivity (Fig. 6B). This behavior is consistent with that reported by Johner et al. [22], De Aguiar et al. [48] and Náthia-Neves et al. [20]. An increase in the S/F ratio results in a longer process time, influencing COM and productivity. Considering COM and productivity, the most appropriate kinetic point to complete the extraction is in the S/F ratio of approximately 13.5 g CO_2/g SB, which corresponds to 11 min of extraction. At this kinetic point of extraction, 70.6% of oil can be extracted. Different percentages of extraction are reported to be economically feasible in the literature depending on the conditions of extraction and raw materials [17,20,36]. Therefore, this kinetic point (S/F of 13.5 g CO_2/g SB) was used for the pilot-scale study, using a proportional scaling-up of the oil recovery for each plant size.

According to the pilot-scale economic simulation, the scenarios in which the 2 × 15 L extraction unit was used were more attractive in terms of COM, ROI, and GM (Table 3) than the scenarios with 1 × 30 L plants. The highest COM was reached for the 2 × 15 L plant in scenarios 2 (US$ 49.21/kg SB oil) and 10 (US$ 105.51/kg SB oil) and for the 1 × 30 L plant in scenarios 3 (US$ 61.90/kg SB oil) and 11 (US$ 124.72/kg SB oil). The COM is smaller in the scenarios for the 2 × 15 L plant. This finding can be attributed to a high versatility and optimization of time when working with two or more extractors in parallel mode. The lowest COM corresponds to normal conditions of plant cost, raw material, wage, and the number of workers (Table 1). Considering 1 × 30 L (scenario 7) and 2 × 15 L (scenario 6) plants, the two-fold increase in the cost of the raw material led to a remarkable increase in COM, which was higher than the scenarios in which double plant costs (scenarios 4 and 5) or double wages and workers (scenarios 8 and 9) were considered. This behavior can be seen in scenarios employing 2 × 15 L and 1 × 30 L plants. It can be inferred that COM was more sensitive to the variation in the price of the raw material, as reported by other authors [36,49].

Table 4 shows a comparison of the contribution of each itemized cost (FCI, CRM, COL, and CUT) on the COM under normal cost conditions for both types of plants. The raw material's purchase value for the extraction process has a higher contribution to the COM than other production costs. The CRM was higher in the 2 × 15 L plants than in the 2 × 1 L and 1 × 30 L plants. This finding is due to its higher productivity (20,083 kg oil/year). The project's sensitivity indicators showed that the ROI was higher for 2 × 15 L plants than for 1 × 30 L plants. The highest ROI was found in the extraction process considering the 2 × 15 L plant, which was 306.3% and corresponds to scenario 2. This value is high and indicates profitability for the project's operation [50,51]. ROI values higher than 80% were reported as indicators of good profitability for a pulp oil production plant's operation from *Caryocar brasiliense* using supercritical technology [22]. An attractive GM of 70.4% was found in scenario 2, which corresponds to the highest ROI. This GM value indicates that approximately 70.4% of the income from SB oil sales would enter the company as gross profit. A value close to the GM of 75% was reported in the Pequi oil extraction project, with a projected sales price of US$ 150.00/kg of oil and productivity of 890,462 kg oil/year [22].

The recovery times for the different evaluated scenarios are shown in Table 3. The recovery time ranged between 0.33 and 1.48 years for the 2 × 15 L plant and between 0.6 and 3.02 years for the 1 × 30 L plant. The scenarios that used the 2 × 15 L plants had the shortest turnaround time compared to the 1 × 30 L extraction unit. These results show that units with more than one extraction vessel operating in parallel are more attractive than units with one vessel extraction. A shorter capital recovery time is always ideal for any investment, although the return time calculated in this study considers the plant to work optimally, that is, without any setbacks. A capital recovery time ranging from 0.6 to 1.5 years was calculated in the project where annatto seeds were processed using a 100 L extraction plant [52]. A longer capital recovery time is consistent with the current findings because larger extraction units require higher capital investment.

An SB oil production plant's design proves to be economically viable when the extraction of approximately 69% of the extractable oil is projected (27 g oil/100 g SB seed). Complete extraction of bioactive compounds is almost always not economically feasible due to the lengthy process time required [53]. A complete extraction does not guarantee higher profitability of the project because the SFE of the last fraction of compounds is generally controlled by the diffusion phenomenon, which increases time, increasing the manufacturing operating costs. A supercritical plant project's profitability must seek a balance

between technical and economic criteria, aiming at higher profitability [20,54].

4. Conclusion

Supercritical CO_2 extraction of SB oil was successful. The best extraction yield (40 g oil/100 g SB seeds) was found at 30 MPa and 40 °C, higher than those reported in the literature. Under this extraction condition, the economic evaluation showed that the best kinetic point was for an S/F of 13.5 g CO_2/g SB seeds. The 2 × 15 L extraction plant was more attractive in economic terms than the 1 × 30 L unit because it is possible to carry out several operations in parallel, which translates into a COM (US $49.21/kg of SB oil) and productivity (20,083 kg of oil/year) approximately 20% more attractive in the normal operating cost scenario. According to the spline model, this kinetic point is found in the FER period, in which the extraction can obtain approximately 69% of the extractable oil (27 g of oil/100 g SB seed). The extracted oil at 30 MPa and 40 °C contained more bioactive compounds than the oil obtained at 20 MPa and 40 °C. The results of supercritical CO_2 extraction of SB oil shown in this study are promising. Nevertheless, further studies targeting application evaluations are needed to apply the oil in cosmetics, functional foods, aromatherapy, and drugs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Artigo 3: **A comparative and economic study of the extraction of oil from baru** (*Dipteryx alata*) **seeds by supercritical co_2 with and without mechanical pressing**

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Research article

A comparative and economic study of the extraction of oil from Baru (*Dipteryx alata*) seeds by supercritical CO_2 with and without mechanical pressing

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ABSTRACT

The present study evaluated the effect of supercritical fluid extraction (SFE) assisted by cold pressing (SFEAP) on the overall yield, extraction kinetics, composition of baru seed oil and manufacturing cost (COM). The best extraction conditions were determined in extraction assays combining different pressures (150–350 bar) and temperatures (35 and 45 °C). The extraction yield by SFEAP (28.6 g oil/100 g baru seed) was approximately 31% higher than that obtained by SFE (21.9 g oil/100 g baru seed), according to the kinetic study with the best extraction conditions (350 bar and 45 °C). The extraction yield observed under this condition allowed us to obtain a lower COM for both techniques (SFE was US$ 118.32/kg baru oil and SFEAP was US$ 87.03/kg baru oil) compared to lower pressures and temperatures. The oil obtained under all extraction conditions was rich in unsaturated fatty acids and other bioactive compounds. The extraction of baru seed oil by SFEAP resulted in a higher yield and lower manufacturing cost than SFE.

1. Introduction

The baru (*Dipteryx alata*) is native to the Brazilian savannah; its seeds are consumed roasted and used as ingredients in the typical gastronomy in several states of Brazil. Baru seeds have high lipid and protein contents of high nutritional qualities (Sousa et al., 2011; Fernandes et al., 2010). In traditional medicine, baru is used to treat various diseases, such as cholesterol, diabetes, gastritis, osteoporosis, and sexual impotence (Ribeiro et al., 2017). Recently, it has been reported that baru seed consumption contributes to the reduction of cholesterol in slightly hypercholesterolemic people (Bento et al., 2014).

Several studies have focused on the extraction and identification of the bioactive compounds present in baru seeds to better use their nutraceutical potential. For this purpose, discontinuous and continuous mechanical pressure was used to extract the oil, obtaining yields of 7.9 % and 25 %, respectively (Marques et al., 2015). The yield obtained in the continuous pressing process was higher than that obtained by discontinuous mechanical pressure (Marques et al., 2015) and SFE (Santos et al., 2016). Nonetheless, in the oil obtained, no terpenes were detected. These are the compounds with the major biological activities present in baru seeds. Therefore, the continuous pressing process negatively affects the composition of the oil due to the temperature increase resulting from friction (Marques et al., 2015). This behavior was different in the oil obtained by hydraulic pressing, in which the presence of mono- and sesquiterpenes was observed but with a lower overall yield (Marques et al., 2015). On the other hand, SFE has been successfully applied for oil extraction of added value nutraceutical from *Vitis vinifera* L. (Coelho et al., 2018), *Eucommia ulmoides* Oliv (Zhang et al., 2018), *Hylocereus polyrhizus* (Abdullah et al., 2018), *Citrullus lanatus var. Colocynthoideis* (Karrar et al., 2019), *Dracocephalum kotscthyi* Boiss *(D. kotschyi)* (Sodeifian et al., 2017), *Plukenetia volubilis* L. (Triana-Maldonado et al., 2017), the pulp *Caryocar brasiliense* (Johner et al., 2018b) and *Persea americana* (Abaide et al., 2017; Corzzini et al., 2017). SFE was applied in the extraction of baru seed oil using supercritical carbon dioxide as the extraction solvent, obtaining the highest yields at 40 °C (22.6 %) and 50 °C (22.8 %) at 35 MPa (Santos et al., 2016).

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These results were obtained using a solvent flow rate of 11.46 g/min and solvent mass/feed mass ratio (S/F, g/g) of 458.4, both used as scaling factors (Duba and Fiori, 2019). In the literature, lower values are used for scaling projects (Prado et al., 2011), and it is known that these factors influence technical and economic viability; therefore, it is necessary to optimize SFE processes at a laboratory scale seeking to obtain the lowest flow rate and S/F possible. The reduction in particle size leads to an increase in the overall extraction yield. Nevertheless, an excessive reduction (such as 0.5 mm as used by Santos et al. (2016)) could cause fluidization and agglomeration problems due to the flow rate of the solvent, producing channels in the extraction bed (Valle, 2015; Valle et al., 2014).

Alternatively, organic solvents could be used as cosolvents in supercritical extraction to improve the extraction yield of baru oil, as was done in the extraction of quinoa oil (Wejnerowska and Ciaciuch, 2018). Nevertheless, it is not attractive for the present study because it affects the extraction selectivity and negatively affects the oil phytochemical profile. Then, the use of cosolvents was not considered because this study aimed to obtain an oil rich in terpenic compounds, which are low polarity compounds such as supercritical CO_2 (Park et al., 2007). An extraction method was recently developed, combining two extraction methods, SFE and cold pressing, called supercritical fluid extraction assisted by pressing (SFEAP) (Johner et al., 2018b). The SFEAP method, compared to SFE, proved to be more efficient in extracting pequi oil (*C. brasiliense*). In that study, the pressure was applied through a piston connected to the extractor; the pressure was generated by applying two torques (40 Nm and 70 Nm). The authors concluded that the lowest torque efficiently increased the extraction yield (Johner et al., 2018b). Similar studies were carried out with fennel (*Foeniculum vulgare*) (Hatami et al., 2018) and clove buds (*Syzygium aromaticum*) (Hatami et al., 2019). In both, an increase in the extraction yield was observed with the SFEAP method with a torque of 40 N.m. The implementation of cold pressing in the SFE process increases the extraction yield and, consequently, decreases the cost. The technique's cost/benefit is also attractive due to the time gain considering that the SFEAP method requires less time (Hatami et al., 2019). For these considerations, the present study aimed to evaluate the interaction between the cold pressing process's extraction pressure and extraction with supercritical CO2 (sc-CO2) on the extraction yield and composition of baru seed oil. Additionally, both extraction processes (SFE and SFEAP) were evaluated economically.

2. Materials and methods

2.1. Sample obtention

A total of 8.4 kg of baru fruit was collected from the soil under trees in the city of Pontal do Araguaia, MT, Brazil. The fruits were then bagged and transported to the Supercritical Technology Laboratory (LASEFI) in Campinas, SP, Brazil.

2.2. Sample preparation

Baru fruits were selected, washed with drinking water, and left to dry at room temperature (20 °C for one day). After drying, the fruits were peeled and pulped manually with the aid of a stainless steel knife, obtaining the endocarp containing the seeds. The seeds were removed by cutting the endocarp using a hand-held metal saw and a bench blade. The seeds were stored at freezing temperature (-20 °C) and protected from light until the extraction experiments were carried out. For the extraction, the baru seeds were previously submitted to grinding using a Mixer (Walita Philips Mix, 400 W, Brazil) for 80 s. The average particle diameter was determined using a sieve shaker (Bertel, N. 1868, Caieiras, Brazil), according to the equation proposed by the American National Standard Institute (ANSI-ASAE, 1998).

2.3. SFE extractions

The extractions were performed on equipment assembled and validated at LASEFI (Johner and Meireles, 2016). In the extraction assays, 10 g of ground baru seeds was used. With an average particle size of 1.8 mm, loaded in a 0.1 L extraction vessel, the vessel's volume not occupied by the sample was completed with glass beads. The extractions were carried out using a static time of 5 min and combining pressures of 150, 200, 250, 300, and 350 bar, with two temperatures of 35 and 45 °C, making a total of 10 extractions, with two repetitions in each assay. The extractions were performed for 17 min (S/F ~ 12), and the yields obtained were used to determine the best extraction pressure and temperature. These conditions were used for the kinetic study until complete extraction. Carbon dioxide was used as the extraction solvent at 99% purity (White Martins, Campinas, Brazil). The extraction yield (y,%) was calculated with Eq. (1), where m_{oil} is the mass of the extracted oil and $m_{raw\text{-}material}$ is the mass of the raw material used for extraction.

$$y(\%) = \frac{m_{oil}}{m_{raw\ material}} \times 100 \quad (1)$$

2.4. SFEAP extractions

The SFEAP method was performed in the same equipment as SFE, to which a cold-pressing system was attached. The extraction process was performed according to the methodology described by Johner et al. (2018b). Ten grams of ground baru seeds were placed in a 0.1 L extraction vessel, and then the sample was compressed with the piston of the cold-pressing system by applying a torque of 40 Nm with the aid of a torque wrench (Sata, ST96303SC, Sorocaba, Brazil). After pressing, the pressing system was disassembled, and the extraction vessel was assembled (Johner et al., 2018b). The best extraction conditions were determined following the same steps and conditions described in section 2.3.

2.5. Extraction kinetics and modeling

The best extraction conditions (pressure and temperature) determined in sections 2.3 and 2.4 were used to obtain the baru oil extraction kinetics by SFE and SFEAP. The extraction kinetics were constructed by plotting the accumulated extraction yield (g) versus the extraction time (min). Approximately 10 g of ground baru seeds was used for extraction, and during the extraction period, 14 extract samples were collected sequentially at different times (approximately 1, 2, 4, 7, 10, 15, 21, 29, 39, 54, 76, 103, 139 and 185 min).

The spline model was used for the mathematical modeling of extraction kinetics by SFE and SFEAP. The spline model typically describes three regions or extraction periods. A period of constant extraction speed (CER) in which the extraction is controlled by convection. A period of decrease in extraction speed (FER) in which extraction occurs by convection and diffusion, and finally, a period controlled by diffusion (DC) (Jesus et al., 2013; Meireles, 2008). The spline model is shown in Eqs. (2), (3), and (4).

$$m_{Ext} = a_1 t;\ t \le t_{CER} \quad (2)$$

$$m_{Ext} = a_1 t_{CER} + a_2 (t - t_{CER});\ t_{CER} < t \le t_{FER} \quad (3)$$

$$m_{Ext} = a_1 t_{CER} + a_2 (t_{FER} - t_{CER}) + a_3 (t - t_{FER});\ t > t_{FER} \quad (4)$$

where m_{Ext} is the mass of extract (g oil baru seeds); a_1, a_2 and a_3 are the slope coefficients (first-order terms) of CER, FER and DC straight lines, respectively (g/min); t_{CER} is the time interval of the CER period (min); and t_{FER} is the end of the FER period (min).

The fit quality of the experimental data to the spline model was evaluated considering the objective function defined as the absolute

average relative deviation (AARD) referred to as the accumulated mass extract expressed by Eq. (5) (Santos et al., 2016):

$$\mathrm{AARD}(\%) = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}}\right| \quad (5)$$

AARD is the average absolute relative deviation (%), n is the number of data points, and xi, exp and xi, and cal refer to the experimental and calculated yields for data i, respectively.

2.6. Extracts analysis

Qualitative analysis of baru oil by thin-layer chromatography (TLC) was performed for the qualitative identification of volatile compounds. Silica gel plates (Macherey-Nagel, DC-Fertigfolien Alugram®, Xtra SIL G, 20 × 20 cm, Germany) were used as a stationary phase. The mobile phase was the same as Santana and Meireles (2016) used to quantify phenolic and volatile compounds. The mobile phase was composed of chloroform, ethanol, and glacial acetic acid (95:05:01 v/v, respectively). The detection of volatile compounds was carried out by spraying the vanillin-sulfuric acid developer on the plate at the concentration described by Pirrung (2017). The images of the revealed TLC plates were measured using ImageJ software, as described by Johner and Meireles (2016).

Baru oil extracted with the best extraction conditions in both methods, SFE and SFEAP, was analyzed to determine its composition in fatty acids. The oil was esterified to obtain fatty acid methyl esters (FAMEs) with approximately 0.5 g of oil, 10 mL of methanol, and two drops of H2SO4 at reflux for 2 h (Hartman, 1973). FAMEs were extracted with hexane and injected into the organic phase in an Agilent 6890 gas chromatograph. The chromatograph was equipped with a Stabilxax column (30 m × 0.25 mm; 0.25 μL) and a flame ionization detector (FID). Helium was used as a carrier gas, and the temperature was programmed as follows: 45 °C for 2 min, 5 °C/min up to 50 °C, 30 °C/min up to 250 °C, isotherm for 10 min. The injector and detector temperatures were adjusted to 250 °C. The identification of fatty acids was carried out by comparing the retention times of FAMEs obtained from baru oils with a FAME standard (Supelco, C8–C24 p/n CRM18918, USA) analyzed under the same chromatographic conditions. Fatty acids were quantified by calculating each FAME's peak area percentages, reporting as a relative percentage (%).

2.7. Process simulation model

The SFE and SFEAP process simulations were performed using SuperPro Designer 8.5® software (Intelligen Inc., Scotch Plains, NJ, USA). Figure 1 shows the flowsheet used for the simulation of the SFE process. The process consisted of a CO_2 replacement inlet, a cooler, a pump, and a heater. Initially, ground baru seeds are loaded into the extractor. Then, CO_2 is cooled (-4 °C) using P2/HX-101 and pressurized (150–350 bar) using P-3/PM-101. CO_2 is heated (35–45 °C) by P-4/HX-103 and enters P-8. Once the temperature and pressure are reached, extraction is performed. The solvent and the extract were recovered using a separation vessel P-13/V-103 (50 °C and 90 bar). The sc-CO_2 is reused through P-5/G-101 (20 °C and 60 bar). For the SFEAP process (Figure 2), the raw material is cold-pressed in P-6/BGBX-101 before entering the extractor. Then, the pressed raw material is loaded into the extractor, and the process is conducted as described previously for the SFE process.

2.8. Economic evaluation

The value of each piece of equipment used in the SFE and SFEAP processes was estimated using direct quotation values reported by Johner et al. (2018c) (see Table 1). An extraction facility with one extraction vessel of 40 L was considered. This volume was chosen based on our experience in the development of homemade SFE equipment. To determine the equipment cost at the required capacity, Eq. (6) was used. This equation corresponds to the power law of capacity (Smith, 2005).

$$C_1 = C_2\left(\frac{Q_2}{Q_1}\right)^n \quad (6)$$

Eq. (6) has been used by several authors to estimate the cost of several types of equipment used to calculate the COM of *Genipa americana* extracts (Náthia-Neves et al., 2019), *Carludovica palmata*, Ruiz & Pav (Galviz-Quezada et al., 2019) and cupuassu extracts (Cavalcanti et al., 2016).where C_1 is the equipment cost with capacity Q_1, C_2 is the known base cost for the equipment with capacity Q_2, and n is the equipment-type constant. Values of n were collected from El-Halwagi (2012) and Peters et al. (2003). In this study, the cost of manufacturing (COM) was estimated according to the method proposed by Turton et al. (2012) (Eq. 7). The three main components (direct costs, fixed costs, and general expenses) were estimated in terms of the following five major costs: fixed capital of investment (FCI), cost of raw material (CRM), cost of

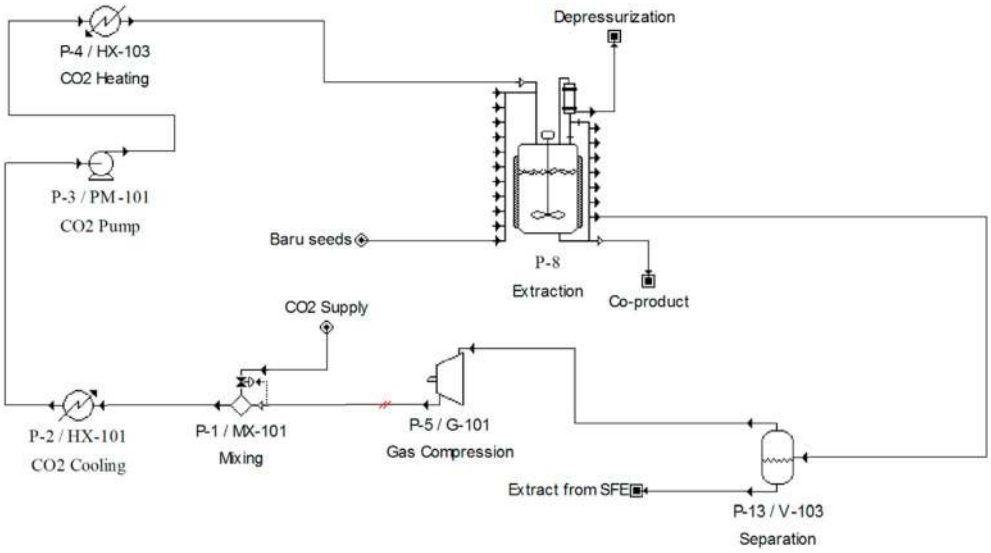

Figure 1. Flowsheet of the SFE process, designed by SuperPro Designer 8.5® software: CO_2 is cooled (-4 °C) using P2/HX-101 and pressurized (150–350 bar) using P-3/PM-101. CO_2 is heated (35–45 °C) by P-4/HX-103 and enters P-8. The solvent and the extract were recovered using a separation vessel P-13/V-103 (50 °C and 90 bar). The sc-CO_2 is reused through P-5/G-101 (20 °C and 60 bar).

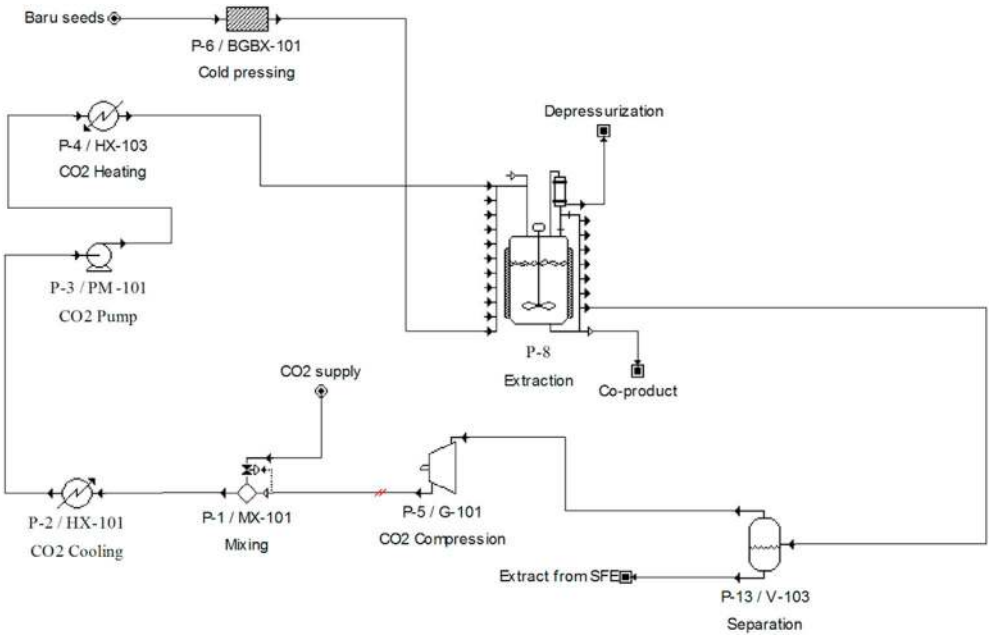

Figure 2. Flowsheet of the SFEAP process, designed by SuperPro Designer 8.5® software. CO_2 is cooled (-4 °C) using P2/HX-101 and pressurized (150–350 bar) using P-3/PM-101. CO_2 is heated (35–45 °C) by P-4/HX-103 and enters P-8. The solvent and the extract were recovered using a separation vessel P-13/V-103 (50 °C and 90 bar). The sc-CO_2 is reused through P-5/G-101 (20 °C and 60 bar).

Table 1. The basic cost for equipment composing the SFE and SFEAP plants.

	n[a]	Unit base cost (US$) 0.1 L[b]	Number required	Total base cost (US$)
Jacketed extraction vessel	0.82	$300.00	1	$40,814.00
Air-driven pump (booster)	0.55	$800.00	1	$21,589.00
Cooler	0.59	$1,360.00	1	$46,640.00
Heater	0.59	$430.00	1	$14,746.00
Separation vessel	0.49	$600.00	1	$11,302.00
Manometer	0.60	$70.00	2	$5,098.00
Blocking valve	0.60	$60.00	2	$4,369.00
Micrometering valve	0.60	$130.00	1	$4,733.00
Safety valve	0.60	$280.00	1	$10,195.00
Flowmeter	0.60	$90.00	1	$3,277.00
Temperature controller	0.60	$180.00	1	$6,554.00
CO_2 compressor	0.46	$1,200.00	1	$18,886.00
Piping, connectors, mixers, splitters, and crossheads	0.60	$250.00	1	$9,103.00
Structural material for supporting the equipment	0.60	$150.00	1	$5,462.00
Total Cost for SFE	-	-	-	**$202,767.00**
Pressing system	0.60	$290.00	1	$10,559.00
Total Cost for SFEAP	-	-	-	**$213,327.00**

[a] n constant depending on equipment type (El-Halwagi, 2012; Peters et al., 2003).
[b] Based on Johner et al. (2018c).

operational labor (COL), cost of utilities (CUT), and cost of waste treatment (CWT).

$$COM = 0.304 \times FCI + 2.73 \times COL + 1.23 \times (CUT + CWT + CRM) \quad (7)$$

FCI is associated with expenses involved in implementing the extraction plant, extractors, equipment, and auxiliary equipment. CRM includes the costs of the preprocessing of the baru seeds for extraction (cleaning, breaking the hard shell, selecting nuts, and milling) and the costs of CO_2. COL is related to the number and wage of the operators of the extraction unit and auxiliary equipment. In this work, two operators were considered to be sufficient based on our experience. CUT considers the energy used in the solvent cycle for generating steam, refrigerating the materials, and using electricity. In this work, CWT is considered to be zero because the coproduct generated from the extraction process is harmless and clean. Thus, it would potentially be used as a raw material in another process, for instance, the baru flour that can be used in the formulation of special diet products.

For scale-up, it was assumed that the process yields and extract composition obtained in the laboratory scale unit would also be obtained at the industrial scale under the same processing conditions. An industrial extractor of 40 L was considered. The SFE and SFEAP processes were designed to operate for 7920 h $year^{-1}$ (e.g., three daily shifts for 330 d $year^{-1}$). The amount of raw material to be extracted was calculated based on the extractor size and the S/F ratio used for the extractions. The

CO_2 loss during the process was presumed to be 2 %, which was the loss from a separator (flash tank) that was calculated by the simulator. Initially, the baru seed purchasing cost was assumed to be US$20 kg^{-1} (Mercadolivre, São Paulo, Brazil). Table 2 provides the data used to estimate COM.

2.9. Sensitivity study

A sensitivity study allows establishing a project's profitability based on project indices and its behavior under different scenarios. The sensitivity study was performed considering that the SFE extract selling price is US$ 533.00 kg^{-1} (Terra Flor, Alto Paraíso de Goiás, Brazil). A sensitivity study is typically conducted using the following project indices: gross margin (GM), return on investment (ROI), payback time (PT), internal rate of return (IRR) and net present value (NPV). The GM is calculated as the percentage of a company's total sales revenue minus its cost of goods sold divided by the total sales revenue. Thus, it is the proportion of each dollar of revenue that the company retains as gross profit (Dimian, 2003). In other words, this parameter is an indicator that allows evaluating the short-term benefits of a specific activity. The ROI is the annual profit generated by a unit of invested capital; then, the more desirable the project is, the higher the ROI. This parameter is a performance measurement used to evaluate the efficiency of an investment. For example, ROI values between 10 % and 15 % are used to accept or cancel a project (El-Halwagi, 2012). PT represents the length of time necessary to recover the cost of an investment. Although the PT's accepted value depends on the type of company and its investors, it is generally accepted that the shorter the payback time is, the faster the initial investment is recovered. The NPV is the difference between cash inflow and cash outflow over a specific period and represents that the remaining "surplus" for the investor is the gain on the initial investment. According to Terry et al. (1992), a project should be considered feasible if the NPV of a project is positive after assuming a discount interest of 7%.

2.10. Statistical analysis

The effect of temperature, pressure, and the extraction method (SFE and SFEAP) on the overall extraction performance was evaluated by analysis of variance (ANOVA) at a significance level of 0.05, considering a full factorial randomized design. The mathematical modeling of the extraction kinetics using Eqs. (2), (3), (4), and (5), was performed using the genetic algorithm (GA) with MATLAB software (MathWorks, version R12).

3. Results and discussion

3.1. Baru fruit and seed characteristics

The production of barú fruits occurs between March and August (Isa, 2009). According to a biometric study of the fruits and seeds, carried out by Zuffo et al. (2014), it was observed that the fruits had a weight between 27.5 and 34.7 g, longitudinal size between 53.7 to 59.5 mm and width between 28.8 to 31.6 mm, on the other hand, the seeds had a weight between 1.2 to 1.3 g, longitudinal size between 22.3 to 25.91 mm and width between 7.2 to 8.9 mm. The seeds present 3.5% moisture, 29.9% protein, 41.9% total lipids, 12.25% carbohydrates and 9.2% total fiber (Sousa et al., 2011). A similar composition was observed by Vera et al. (2009).

Table 2. Input economic parameters used for simulating the COM of Baru oil obtained from Baru seeds by SFE and SFEAP; the scale of 40 L.

	Values
Direct Fixed Capital (DFC)	
SFE extraction plant[a]	US$382,859.00
SFEAP extraction plant[a]	US$400,014.00
Insurance[d]	1.5% DFC
Local taxes[d]	2.5% DFC
Factory expense[d]	5.5% DFC
Fixed capital investment (FCI)	
SFE extraction plant[b]	US$202,767.00
SFEAP extraction plant[b]	US$213,327.00
Depreciation rate[c]	US$ 10%/year
Annual maintenance rate[c]	6%/year
Cost of operational labor (COL)	
Wage[d]	US$ 16.80/h
Number of workers per shift	2.00
Cost of raw material (CRM)	
Baru seeds[e]	US$ 20.00/kg
Pre-processing Baru seeds[d]	US$ 40.00/t
Industrial CO_2[d]	US$ 2.70/kg
Cost of utilities (CUT)	
Electricity[d]	US$ 0.50/kWh
Water (for cooling and cleaning)[d]	US$ 1.06/t
Glycol solution[d]	US$ 15.00/t

[a] SuperPro Designer.
[b] Estimated cost using Eq. (1).
[c] Based on Peters et al. (2003).
[d] based on Johner et al. (2018c).
[e] Direct quotation.

3.2. Oil extraction

ANOVA showed that the temperature, pressure, and extraction method individually had a significant effect (p-value <0.001) on the extraction yield, as observed in the extraction isotherms (Figure 3A). In the same way, the interaction between temperature - pressure and temperature - extraction method showed a significant effect (p-value < 0.02 and p-value < 0.001, respectively). This was different in the interaction between the extraction method and pressure, showing a p-value > 0.05, in the same way, in the interaction between the three variables (p-value > 0.05). These results may be influenced by the highest standard deviation observed in the extraction isotherms of the SFEAP method. This variation in the standard deviation is because, in the SFEAP process, there are losses of extract and raw material, specifically in the disassembly of the mechanical press after mechanical cold pressing. The losses of extract and raw material are because these adhere to the inaccessible spaces of the press piston. These losses could be reduced if the mechanical pressing and supercritical extraction processes were executed online, with which it could avoid such losses.

The highest and lowest yields obtained after 17 min of extraction by SFE were 8.3 g oil/100 g baru seed (350 bar and 45 °C) and 1.9 g oil/100 g baru seed (150 bar and 45 °C), while via SFEAP, they were 12.9 g oil/100 g baru seed (350 bar and 45 °C) and 4.1 g oil/100 g baru seed (150 bar and 35 °C), respectively. The extraction isotherm of SFEAP at 45 °C showed the highest extraction yields compared to the same technique at 35 °C and for SFE at the two temperatures studied (Figure 3A). The effect on baru oil extraction yield, observed under different extraction conditions, is because temperature and pressure affect the properties of sc-CO_2 (Figure 3B), changing its density in the extraction bed (Cornelio-Santiago et al., 2017; Gustinelli et al., 2018; Rai et al., 2018). Overall, the SFEAP technique obtained higher yields in all pressure and temperature conditions than SFE, and the major extraction yield found for baru seeds using SFEAP was 55 % higher than the best result found by SFE at 350 bar and 45 °C. This condition was chosen as the best condition for the kinetic study.

3.3. Kinetic and spline model

The extraction kinetics with the best extraction conditions (350 bar and 45 °C) with SFEAP (29 g oil/100 g baru seed) showed a higher final extraction yield than SFE (22 g oil/100 g baru seed) after approximately 185 min (Figure 4). The extraction yield by SFEAP was 27% higher than that reported by Santos et al. (2016); these results are promising for industrial applications. At 39 min of extraction with the SFEAP technique, an extraction yield similar to that obtained at 185 min of extraction with SFE was obtained using the same pressure and temperature conditions. The higher yield observed in the extraction with SFEAP concerning SFE (Figure 4) can be explained by the effect produced by applying mechanical pressure, which led to a greater release of the oily extract contained in the particles of baru seeds. This produced a greater saturation of the solvent in the static time (5 min), which led to a greater extraction in less process time. Similar observations were noted by Johner et al. (2018b) and Hatami et al. (2018) in the extraction of pulp *Caryocar brasiliense* and seeds *Foeniculum vulgare*, respectively.

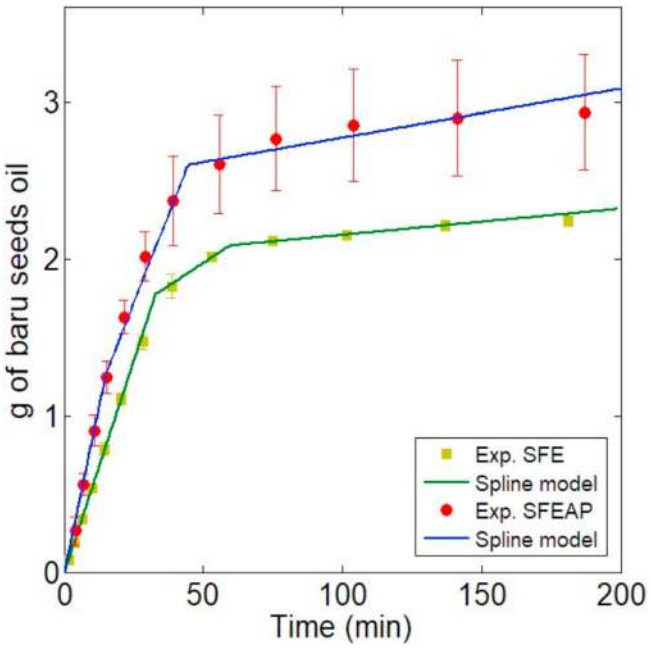

Figure 4. Kinetics of baru seed oil extraction by supercritical CO_2 at 350 bar and 45 °C, with (SFEAP) and without pressing (SFE).

The mathematical model of the extraction kinetics for both the SFE and SFEAP techniques, using the spline model, allowed us to observe three extraction periods, CER, FER and DC. The kinetic parameters of the spline model for the SFE technique were t_{CER} = 32.94 min, t_{FER} = 59.43 min, a_1 = 0.0539 g/min, a_2 = 0.0116 g/min and a_3 = 0.0017 g/min.

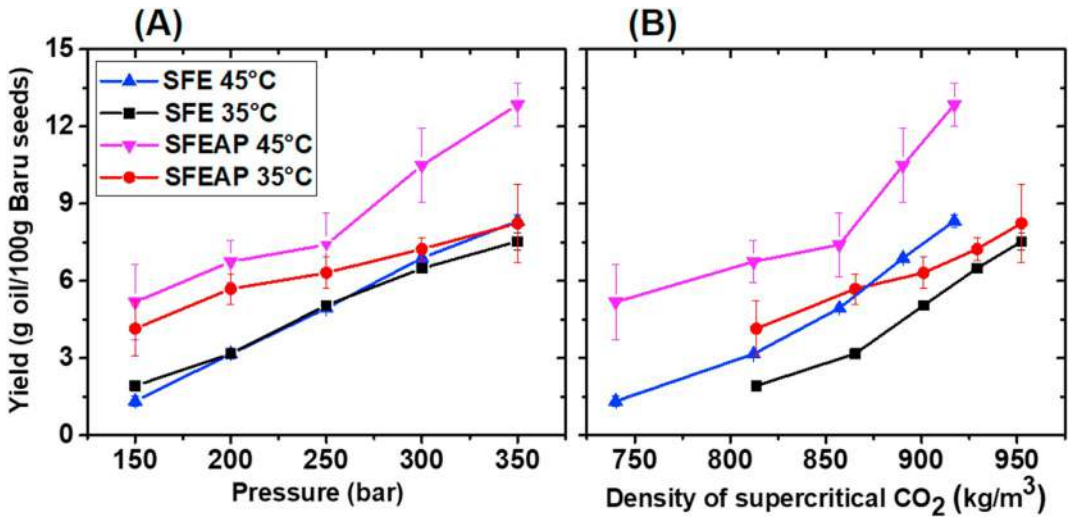

Figure 3. Extraction yield of Baru seed oil with sc-CO_2 at different pressures (150–350 bar). (A) and densities (740.05–952.25 kg m^{-3}) (B), with (SFEAP) and without pressing (SFE) at 35 and 45 °C. The CO_2 flow rate was 7 g/min, and the S/F ratio was 12.

ARRD (%) = 4.7 %. The kinetic parameters of the spline model for the SFEAP technique were t_{CER} = 14.94 min, t_{FER} = 44.44 min, a_1 = 0.0844 g/min, a_2 = 0.0453 g/min and a_3 = 0.0031 g/min. ARRD (%) = 5.11 %. The yield in the CER period for the SFEAP technique (12.61 g oil/100 g baru seeds) was lower than that of the SFE technique (17.75 g oil/100 g baru seeds). In the FER period, the yield obtained by SFEAP (25.97 g oil/100 g baru seeds) was higher than that obtained by SFE (20.83 g oil/100 g baru seeds). The modeling of the extraction kinetics by SFE reported by Santos et al. (2016) showed, for the same raw material, two extraction periods according to the spline model. For the CER period (t_{CER} = 11.46 min), they reported a 20.11% mass yield, with a mass transfer rate (m_{CER}) of 0.61 g/min. These differences from our study are probably due to the smaller particle size (0.508 mm) and higher CO_2 flow (11.46 g/min) used by these authors; it is known that a greater decrease in particle size and a higher CO_2 flow increase the extraction yield (Johner et al, 2018a, 2018c). However, it is recommended for industrial purposes to use particular sizes equal to or greater than 1 mm to avoid fluidization and channeling problems of the extraction bed (Valle et al., 2014; Valle, 2015).

The yield in the FER period (44.44 min) obtained by SFEAP (25.97 g oil/100 g baru seeds) was higher than the total yield (22.8 g oil/100 g raw material) obtained in 120 min of extraction by Santos et al. (2016). In our study, extraction by SFEAP turned out to be more efficient than extraction by SFE, observing a higher yield in the FER period and, thus, for the total extraction time. This can be explained by observing that higher mass transfer rates were obtained for the three extraction periods. The mechanical pressure used in the SFEAP technique allows a greater release of the substrate, which leads to saturation of the extraction bed before supercritical extraction, allowing a higher extraction yield (Hatami et al., 2018; Johner et al., 2018b).

3.4. TLC

The baru oil extracts obtained under different conditions (pressure, temperature and extraction technique (SFE and SFEAP)) have similar phytochemical profiles (Figure 5), showing two spots on both chromatoplates, SFE (Rf, 1 = 0.35 and Rf, 2 = 0.65) and SFEAP (Rf, 1 = 0.31 y Rf, 2 = 0.61). The extracts obtained via SFEAP indicated an Rf of 0.31 compounds that were only indicated in SFE 150 bar and 35 °C. The purple spots on the chromatoplate indicate the presence of terpenoids (Tirimanna, 1973; Wagner et al., 1984). This coloration is produced by derivatization with the chromogenic reagent vanillin + sulfuric acid (Santana and Meireles, 2016; Spangenberg et al., 2011). Under the best extraction conditions (35 MPa and 45 °C) for both techniques (SFE and SFEAP), SFEAP showed two spots on the chromatoplate, and SFE showed only one (Figure 5), which allows us to infer that the SFEAP technique improved the composition of bioactive compounds.

3.5. Fatty acid composition

The fatty acid profile and composition of baru oil obtained under the best extraction conditions (35 MPa and 45 °C) for both techniques (SFE and SFEAP) were similar (Table 3). A similar effect was observed for the fatty acid profile of *Caryocar brasiliense* oil obtained by both techniques (Johner et al., 2018b). The fatty acid composition of baru oil observed in the present study was similar to that reported by Santos et al. (2016). Baru oil contained 5 saturated fatty acids (C16:0, C18:0, C20:0, C22:0 and C24:0), 3 monounsaturated fatty acids (C18:1, C20:1 and C22:1) and a polyunsaturated fatty acid (C18:2). The content of monounsaturated fatty acids (MUFAs) was larger than the contents of polyunsaturated (PUFA) and saturated (SFA) fatty acids. An important concentration of MUFAs and PUFAs is noteworthy, especially linoleic fatty acids (omega 6), which, on average, showed a concentration of 26.5%. This polyunsaturated fatty acid is not synthesizable by humans. Therefore, it must be supplied through the foods that contain them. Its consumption is of great importance due to specific functions in which it participates: regulating monocyte immunomodulation related to atherosclerosis (Subash-Babu and Alshatwi, 2018), in combination with other PUFAs it has an anti-inflammatory effect (Melo et al., 2017), it has a cardioprotective effect (Chattipakorn et al., 2009), regulating metabolic syndrome in adults (Mirmiran et al., 2012) and other effects on human health.

3.6. Economic evaluation

Initially, the COM was determined for different process conditions for both processes. Processes with an S/F of 12 and pressures between 150 and 350 bar and temperatures of 35 and 45 °C were tested to compare the extraction process based on the COM. As can be observed in Table 4, for both extraction processes, the COM decreased as the pressure increased at the same temperature. Similar behavior was observed when the temperature increased. The combination of higher temperatures and pressures enhanced the performance of the process, and the yield increased. As the COM is calculated as the relation between the annual operating cost (CMR + FCI + COL + CUT) and the annual production rate, in this case, as the annual operating cost is almost constant for all process conditions (Table 4), the higher the yield is, the higher the productivity and therefore the lower the COM. A higher yield was obtained for both extraction processes when the process was conducted at 45 °C and 350 bar. Under these process conditions, COMs of US$ 260.33 kg^{-1} baru oil and US$ 167.77 kg^{-1} baru oil were determined for SFE and SFEAP, respectively. These COMs are consistent with the literature. For example, under optimized conditions, the SFE COMs were US$ 125.41 kg^{-1} and US$ 178.8 kg^{-1} for the production of oleoresin from malagueta peppers (Aguiar et al., 2018) and turmeric (Carvalho et al., 2015).

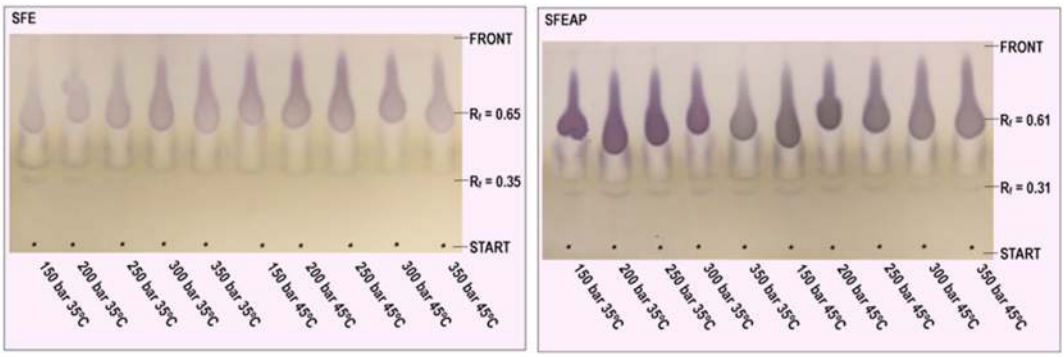

Figure 5. Images of the chromatoplates obtained from Baru oils obtained by SFE and SFEAP visualized under visible light after post derivatization with vanillin-sulfuric acid. Mobile phase: chloroform:ethanol:glacial acetic acid (95:05:01 v/v, respectively).

Table 3. Fatty acid composition (%) of Baru oil obtained by SFE (350 bar and 45 °C) and SFEAP (350 bar and 45 °C).

Fatty acid	SFE (350 bar–45 °C)	SFEAP (350 bar–45 °C)
Palmitic acid (C16:0)	7.6 (±0.1)	7.3 (±0.1)
Stearic acid (C18:0)	5.7 (±0.1)	5.7 (±0.1)
Oleic acid (C18:1)	50 (±1)	49 (±1)
Linoleic acid (C18:2)	27 (±1)	26 (±1)
Arachidic acid (C20:0)	1.4 (±0.1)	1.4 (±0.1)
cis-11-Eicosenoic acid (C20:1)	2.9 (±0.1)	2.9 (±0.1)
Docosanoic acid (C22:0)	3.0 (±0.1)	3.6 (±0.1)
Erucic acid (C22:1)	0.30 (±0.01)	0.38 (±0.01)
Lignoceric acid (C24:0)	2.6 (±0.1)	3.5 (±0.1)
SFA	20.3 (±0.5)	21.5 (±0.5)
MUFA	53 (±1)	52 (±1)
PUFA	27 (±1)	26 (±1)

Table 4. COM composition and project indices of the SFE and SFEAP processes. The system capacity and the Baru seeds purchasing cost were 40 L and US$ 20 kg^{-1}, respectively.

Pressure (bar)	Temperature (°C)	COM (US$/kg)	CRM (%)	COL (%)	FCI (%)	CUT (%)	GM (%)	ROI (%)	PT (years)	IRR (%)	NPV (US$ x 10^6)
SFE process											
150	35	1123.57	95.67	1.9	1.23	1.19	-110.8	-347.74	N/A	N/A	-26.68
200	35	681.97	95.61	1.9	1.23	1.26	-27.95	-142.73	N/A	N/A	-11.43
250	35	428.47	95.54	1.9	1.23	1.33	19.61	100.86	0.99	81.17	6.77
300	35	333.66	95.48	1.9	1.23	1.39	37.4	242.58	0.41	161.02	17.34
350	35	287.63	95.42	1.9	1.23	1.46	46.04	345.13	0.29	205.86	24.99
150	45	1628.96	95.61	1.9	1.23	1.26	-205.62	-446.1	N/A	N/A	-34.03
200	45	684.17	95.54	1.9	1.23	1.33	-28.36	-144.45	N/A	N/A	-11.56
250	45	438.14	95.48	1.9	1.23	1.4	17.8	89.89	1.11	73.67	59.56
300	45	314.69	95.41	1.9	1.23	1.46	40.86	281.23	0.36	178.83	20.23
350	45	260.33	95.35	1.9	1.23	1.53	51.16	423.15	0.24	235.39	30.83
SFEAP process											
150	35	518.05	96.25	1.53	1.02	1.2	2.8	15.15	6.6	11.95	0.44
200	35	378.05	96.18	1.53	1.02	1.27	29.07	178.59	0.56	133.05	15.05
250	35	340.69	96.12	1.53	1.02	1.33	36.08	244.96	0.41	168.83	20.97
300	35	297.24	96.05	1.53	1.02	1.4	44.23	343.14	0.29	214.14	29.73
350	35	261.36	95.99	1.53	1.02	1.47	50.96	448.89	0.22	256.02	39.18
150	45	415.13	96.18	1.53	1.02	1.27	22.11	124.56	0.8	99.77	10.24
200	45	318.7	96.11	1.53	1.02	1.34	40.21	291.28	0.34	191.02	25.10
250	45	290.67	96.05	1.53	1.02	1.4	45.47	360.55	0.28	221.33	31.29
300	45	205.37	95.98	1.53	1.02	1.47	61.47	687.56	0.15	334.3	60.47
350	45	167.77	95.92	1.52	1.02	1.54	68.52	937.44	0.11	401.33	82.79

When both processes are compared, the SFEAP′ COM is lower than the SFE′ COM, as shown in Table 4: for the best process conditions (45 °C and 350 bar), the SFEAP′ COM is almost 35 % lower than the SFE' COM. Generally, the SFEAP process has better performance using a slightly longer extraction time. The SFEAP process lasts only 10 min longer than the SFE process because the SFEAP includes cold pressing in its process. The application of cold pressing in the SFEAP process is fast and straightforward and allows us to increase productivity. As mentioned before, the annual operational cost is almost constant; it is possible to diminish the COM by increasing the extraction yield. Table 4 shows the COM components, and as can be observed, all COM components are similar for both extraction processes.

Moreover, the CMR is the component that has a major contribution to the COM, as has been repeatedly shown in the literature (Johner et al., 2018c; Viganó et al., 2017; Zabot et al., 2018). In this work, the raw material's high price significantly impacted the COM, being responsible for up to 96% of the COM. The raw material (baru seeds) used for the extraction is expensive when compared with other works. For example, the price of the baru seeds used initially (US$ 20 kg^{-1}) is larger than that of passion fruit rinds (US$ 2.7 kg^{-1}) (Viganó et al., 2017), cupuassu seed byproducts (US$ 2.7 kg^{-1}) (Cavalcanti et al., 2016), Capsicum pepper (Aguiar et al., 2018) or even the raw material cost is considered zero if it is a coproduct (Guindani et al., 2016).

In this kind of process, the COM is strongly dependent on the cost of raw material, and thus, this component has an important contribution to the COM of the extract. Thus, to diminish the COM of the product, it is important to obtain baru at a lower cost, making it possible to improve the baru production chain. In this context, five different scenarios were tested considering lower prices for the baru seeds. Figure 6 shows the influence of the raw material price on the COM for the two studied processes. The behavior of the COM is similar in both extraction processes. As expected, the lower the raw material cost, the lower the COM obtained. For example, under the best process conditions, when the raw material price decreased from US$ 20 kg^{-1} to US$ 10 kg^{-1}, COM decreased from US$ 260.33 kg^{-1} baru oil to US$ 140.31 kg^{-1} baru oil (SFE) and from US$ 167.77 kg^{-1} baru oil to US$ 89.96 kg^{-1} baru oil

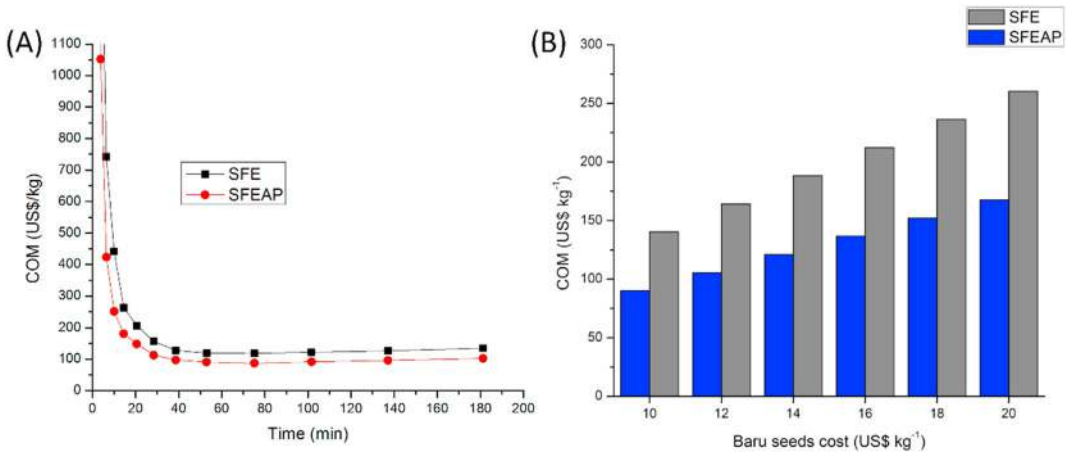

Figure 6. Influence of extraction time and baru seed purchasing cost on the COM for SFE and SFEAP processes. (A): Lines black refer to SFE and lines red to SFEAP. (B): Gray columns refer to SFE and blue columns to SFEAP.

(SFEAP). This is almost two times smaller than the COMs obtained using the original raw material cost.

On the other hand, as shown in Figure 6A, the COM was higher for both extraction processes at the beginning of the extraction. This behavior can be explained by the fact that at short extraction times, it is possible that raw material still retains a considerable amount of Baru oil. On the other hand, when the COM of baru oil is expressed as a function of processing time (Figure 6A), the COMs of SFEAP are lower than the COMs of SFE for all extraction times. Moreover, although t_{FER} is a good parameter for making an initial COM estimate (Turton et al., 2012), according to the economic analysis, for both extraction processes, the lowest production cost was achieved after a processing time of approximately 75 min (Figure 6A). At this extraction time, the COMs obtained were US$ 118,32 kg^{-1} baru oil and US$ 87,03 kg^{-1} baru oil for SFE and SFEAP, respectively.

3.7. Sensitivity study

When both processes are compared, it is observed in Table 4 that when temperature and pressure increased, the project indices (GM, ROI, PT, IRR, and NPV) improved. As mentioned before, the higher the yield, the lower the COM, and therefore, the more feasible the process is. However, for the SFE process, only when the process is performed using pressures above 250 bar will the process be economically feasible, and the economic parameters of the sensitivity study become positive. On the other hand, for the SFEAP process, the process is feasible for all the extraction conditions tested. Thus, the SFEAP process is economically more feasible than the SFE process. Under the lower COM conditions (45 °C/350 bar), the GM of the SFEAP is 25% higher than the GM of the SFE, which means that the company would retain up to US$ 0.69 from each dollar generated instead of US$ 0.51. The same behavior was observed in the other project indices. For example, although the PT for both processes is quite attractive, in the SFEAP process, the initial investment is recovered in 50% less time. On the other hand, the SFEAP process has ROI, IRR, and NPV values 2.2, 1.7, and 2.7 higher than those of the SFE process; thus, although both processes have acceptable and attractive project index values, the SFEAP is the more desirable project.

As stated before, the CWT was considered zero; however, due to the coproduct characteristics, such as its protein content, it could be considered revenue. Therefore, if the coproduct can be sold, the project will be more feasible. In that context, the coproduct selling price ranged between US$ 5 kg^{-1} and US$ 15 kg^{-1}. Figure 7 shows the effect of the coproduct selling price on the project indices. As shown in Figure 7, the SFEAP process's behavior is better than that of the SFE process for all project indices. For example, for GM, it is clear that the higher the selling price of the coproduct is, the lower the GM. In this case, if the company sells the coproduct using the lower selling price (US$ 5 kg^{-1}), the GM is 56.78 % and 70.88 % for the SFE and SFEAP processes, respectively. On the other hand, when the higher selling price is used, the GM for the SFE process is 64.86 % and 74.64 % for the SFEAP process. For both processes, according to the GM, the project is quite attractive because the company would retain at least US$ 0.56 or US$ 0.64 from each dollar generated if the coproduct is sold using the lower price.

Similar behavior was observed for ROI, IRR, and NPV. For example, the higher the coproduct selling price is, the higher the ROI (Figure 7c). Both processes showed excellent behavior regarding the ROI because generally, a minimum value of 15% is assumed to accept a project. In this work, although the coproduct was sold using the less expensive price, ROIs of 529% and 1047% were found for the SFE and SFEAP processes, respectively. On the other hand, the higher a project's IRR is, the more desirable the project; again, although both processes have positive and attractive IRR values, the SFEAP process has better profitability. As shown in Figure 7d, all IRR values in the SFEAP are higher than those in the SFE process, and as the coproduct selling price increases, the IRR increases. For example, when the process was simulated using a coproduct selling price of US$ 5 kg^{-1}, the IRR of the SFEAP is almost 50% higher than the IRR of the SFE process.

Similarly, Figure 7e shows that the higher the coproduct selling price is, the higher the gain on the initial investment for both processes. In this case, the NPV, after assuming a discount interest of 7 % of the SFEAP, is 2.4 times higher than the NPV of the SFE process using the lower coproduct selling price. An increase in the coproduct selling price allows for obtaining a more desirable project. For example, in the SFEAP process, when the coproduct selling price increased from US$ 5 kg^{-1} to US$ 15 kg^{-1}, the NPV increased from US$ 92,652,528 to US$ 112,362,955, which represents 21% more earnings. Contrary to the other project indices, a decrease in the PT was observed when the coproduct selling price increased (Figure 7b). When the coproduct selling price increases, the company generates more revenues, and thus, the length of time necessary to recover the initial investment is shorter. Although the PT is quite acceptable in all scenarios tested in the SFEAP process, the initial investment is recovered almost half of the time. For example, when a higher coproduct selling cost is used, the initial investment is recovered 63 % faster in the SFEAP process than in the SFE process.

In summary, according to the results obtained after the simulations of the different scenarios, it was possible to observe that the project indices are acceptable, and the extraction of baru oil is economically feasible. CRW represents the major contribution to COM; therefore, the raw material cost is a critical factor in the extraction of baru oil. On the other hand, selling the coproduct increases the process's profitability, as shown after the simulation of different sensitivity study scenarios.

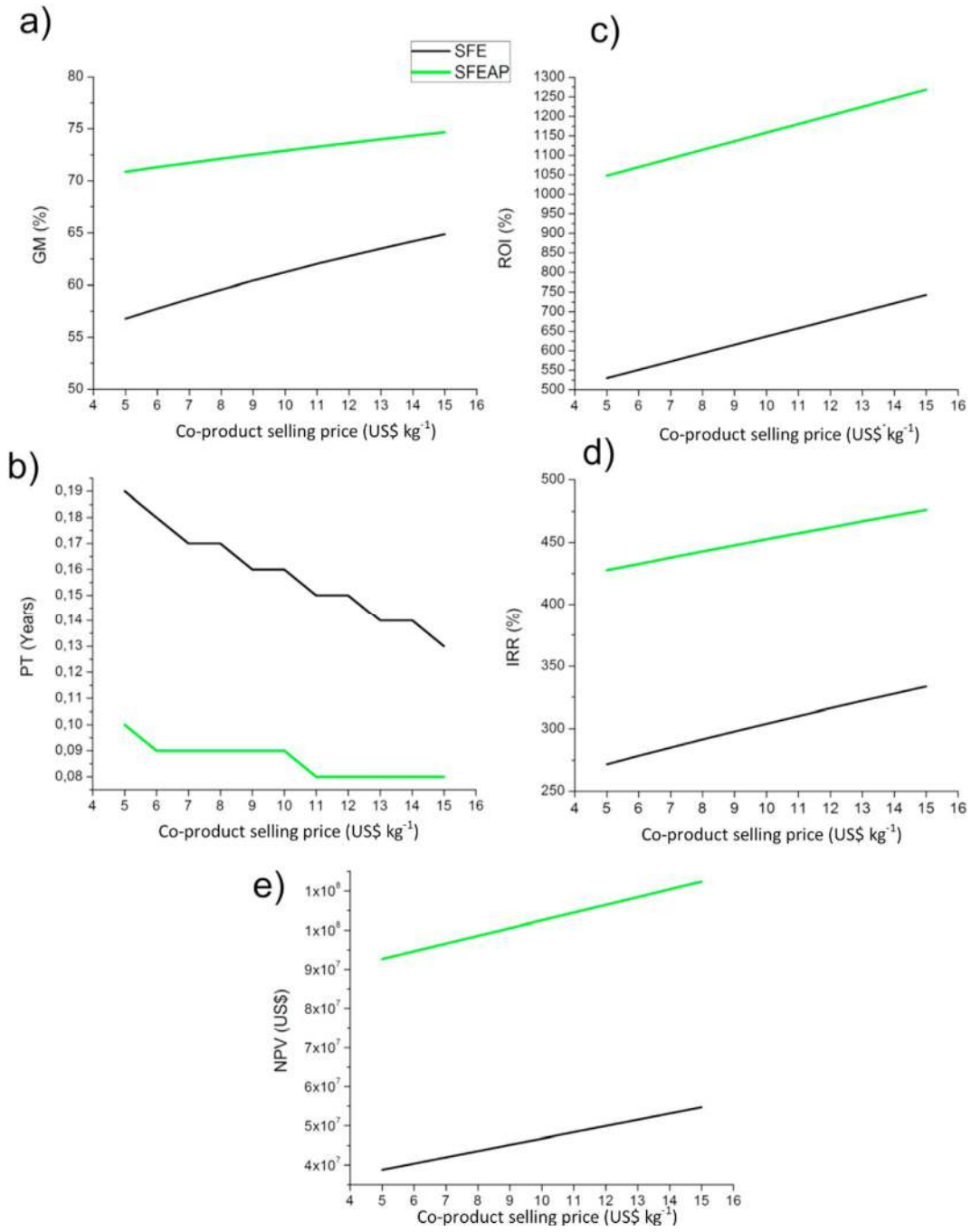

Figure 7. Influence of the coproduct selling price on the SFE and SFEAP processes' project indices. a) to e): Black lines refer to SFE and green lines to SFEAP.

4. Conclusions

Overall, the SFEAP technique obtained higher yields in all pressure and temperature conditions when compared to SFE. Under the best extraction conditions (350 bar and 45 °C), the oil yield of baru seeds using SFEAP (29 g oil/100 g baru seeds) was 31.8% higher than the best result found for the SFE (22 g oil/100 g baru seeds) technique after approximately 185 min of extraction. The extraction kinetics of SFE and SFEAP were adequately modeled by the spline model, observing three extraction periods (CER, FER, DC), with a higher mass transfer rate in the periods of SFEAP extraction compared to SFE. The SFEAP resulted in a promising industrial application technique due to the higher extraction yield and the lower CO_2 flow (7 g/min) used in this study compared to that reported in the literature. The manufacturing cost decreased when the extraction pressure and temperature increased due to the higher oil yield resulting from the increase in pressure and temperature. The most attractive COM was observed in the extraction process at 350 bar and 45 °C for both techniques, SFE and SFEAP. The lowest estimated COM values for the SFE and SFEAP were US$ 118.32/kg baru oil and US$ 87.03/kg baru oil, respectively, when the CRM was US$ 10.0/kg baru seeds. Therefore, the SFEAP process is more economically viable than the SFE, with more attractive project indices. The baru oil obtained by the two techniques was rich in unsaturated fatty acids and bioactive compounds. Both techniques were economically viable for the oil extraction process from baru seeds, but further studies are necessary to fully use the seed on an industrial scale.

Declarations

Author contribution statement

Larry Oscar Chañi-Paucar: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

J. Felipe Osorio-Tobón: Analyzed and interpreted the data; Wrote the paper.

Júlio C. F. Johner: Performed the experiments; Analyzed and interpreted the data.

Maria Angela A. Meireles: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare the following conflict of interests: Maria Angela A. Meireles is an Associate Editor for the Food Science and Nutrition section.

Additional information

No additional information is available for this paper.

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CAPÍTULO IV: *Extração Simultânea com Dióxido de Carbono Supercrítico e Prensagem Mecânica a Frio*

Artigo 1: **Simultaneous integration of supercritical fluid extraction and mechanical cold pressing for the extraction from Baru seed**

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Simultaneous integration of supercritical fluid extraction and mechanical cold pressing for the extraction from Baru seed

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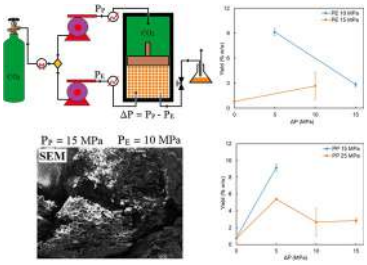
HIGHLIGHTS

- A unit was built that integrates supercritical fluid extraction and mechanical cold pressing, both operating simultaneously.
- The unit showed a good performance for the extraction of oil from the baru seeds.
- The highest yield of 25.1% w/w was obtained at piston pressure of 15 MPa and extraction pressure of 10 MPa.

GRAPHICAL ABSTRACT



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ABSTRACT

Supercritical fluid extraction (SFE) assisted by cold pressing (SFEAP) was previously reported in the literature for oleaginous raw materials to improve the SFE process, but it suffers from operational disadvantages due to its sequential, instead of simultaneous, extraction operations. Therefore, this study aimed to address this issue by simultaneous integrating of SFE and mechanical cold pressing. This new extraction unit, which is called sCO_2 + MCP, was successfully examined for the extraction of oil from Baru seed (BS) under the extraction pressure from 10 to 30 MPa and piston pressure from 10 to 30 MPa. The highest extraction yield (25.1% w/w) obtained by a combination of piston pressure of 15 MPa and an extraction pressure of 10 MPa. The main advantage of the sCO_2 + MCP unit over SFE and SFEAP units is significantly reducing extraction pressure from 35 MPa to 10 MPa.

1. Introduction

The extraction of bioactive compounds using supercritical carbon dioxide (sCO_2) is the most common and widespread application of supercritical technology [1–5]. sCO_2 is presented as a better alternative for the production of bioactive than organic solvents; this is mainly due to its higher selectivity, shorter extraction time, higher efficiency, and easily and completely separating of extracts from solvents [6,7]. The sCO_2 extraction process, from its development to the present, has undergone different modifications. Among them, we can highlight three types of modifications: 1) modifications based on the extraction solvent, 2) modifications based on the raw material, and 3) modifications based

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on extraction equipment.

In the first type of modification, the polarity of sCO_2 is improved using a non-toxic co-solvent such as water or ethanol for polyphenol extraction [8,9] as an alternative to the conventional extraction process [10]. The modifier concentration is strongly depended on the raw material and the type of modifier [8,11]. About the second type of modification, it is reported that using raw material with small particle size and applying enzymes to the raw materials before SFE have positive impact on the extraction performance of volatile compounds [12,13] and polyphenols [14], respectively. Regarding the modifications of the extraction equipment, we can find two recent modifications in the literature; SFE assisted by ultrasound (UASCE) [6,15–17] and SFE assisted by cold pressing (SFEAP) [18–20]. The UASCE applied to cucurbitacin E of *Iberis amara* seeds, and resulted a yield similar to the extraction with acetone (8.6 mg/g), but it reduced the extraction time from 6 to 1 h, liquid/solid ratio from 50 to 30 mL/g, and temperature from 333.15 to 323.15 K [6]. A comparison of SFEAP with SFE showed that it increased the extraction yield of pequi oil from 53% to 55% w/w [20], the volatile oil of clove buds from 21% to 22% w/w [18], and fennel oil from 9.8% to 12% w/w [19]. Although these extraction yields are not markedly different (except for fennel), the SFEAP method decreased the extraction time significantly because the extraction, due to availability of solute on the seed surface, is mainly controlled by convection instead of diffusion [18–20]. Other modifications of the extraction equipment have been reported in the form of patents, in general, these documents describe the modification of the extraction vessel, implementing a multilayer system that allows a self-compression of the raw material inside the extraction vessel [21,22] and a filter device inside the extraction vessel to increase the contact area of the fluid with the solid matrix [23].

We recently studied the application of SFE and SFEAP for the extraction of baru seed (BS) oil under 35 MPa, 318.15 K, and CO_2 flow rate of 7 g/min, obtaining the yields of 21.9 for SFE and 28.6% w/w for SFEAP [24]. The SFEAP is executed in two stages. The raw material is subjected to mechanical pressing with a device coupled to the extraction container in the first stage. In the second stage, the pressing device is disassembled from the extraction vessel to start the extraction process with sCO_2. Despite the higher performance of SFEAP compared to SFE, the extract is exposed to the environment while switching from pressing to SFE that may deteriorate the compounds of interest. Moreover, assembling and disassembling the pressing device is a big challenge from the industrial perspective as it requires extra time and costs. Therefore, the main objective of this study was to design, built, and evaluate a new extraction unit that allows simultaneous operation of sCO_2 extraction and mechanical cold pressing, applied to the extraction of oil from baru (*Dipteryx alata*) seeds. To this end, the extraction unit employed two streams of sCO_2, one of which was used as a hydraulic fluid to exert mechanical pressure on the raw material, and the other stream was used as the extraction solvent. The results show that the new extraction unit reduces the extraction pressure significantly in comparison with the pressures used in SFE and SFEAP for BS.

2. Material and methods

2.1. Sample

BS was purchased from a local supplier in Pontal do Araguaia, MT, Brazil. BS were ground for 80 s using a Mixer (Walita Philips Mix, 400 watts, Brazil), as in our previous work [24]. Ground seed samples were stored at approximately 253 K, protected from light until extraction experiments. The mean diameter of the BS particles after grinding was determined according to the American National Standard Institute [25].

2.2. Moisture content and ether extract

The ground BS was firstly subjected to an oven at 378 K, and is periodically weighted along the drying. This process is continued until the BS weight remain constant. The moisture content of the sample is equal to the difference between the initial and final BS weight [26]. The dry sample was then subjected to extraction by Soxhlet with ether at 378 K for 8 h. The obtained ether extract was weighed and analyzed to calculate the samples' total lipid (or ether extract) content [26].

2.3. Apparent and real density

The apparent density of the particle bed was determined by dividing the total mass of a sample quantity by the volume occupied by the same mass. The real density was measured in a helium gas pycnometer (AccuPyc 1330 V2.02, 2399) at the Calibration and Analytical Resources Laboratory/UNICAMP, Campinas, Brazil. Before the analysis, the sample's humidity was conditioned in a vacuum oven at 318 K for 24 h. The real density analysis was performed for the samples before and after the extraction.

2.4. Particle bed porosity (ε)

The porosity of the bed was calculated using Eq. (1).

$$\varepsilon = 1 - \frac{\rho_a}{\rho_r} \tag{1}$$

Where ρ_a is the apparent density, and ρ_r is the density of solid material.

2.5. Scanning electron microscopy (SEM)

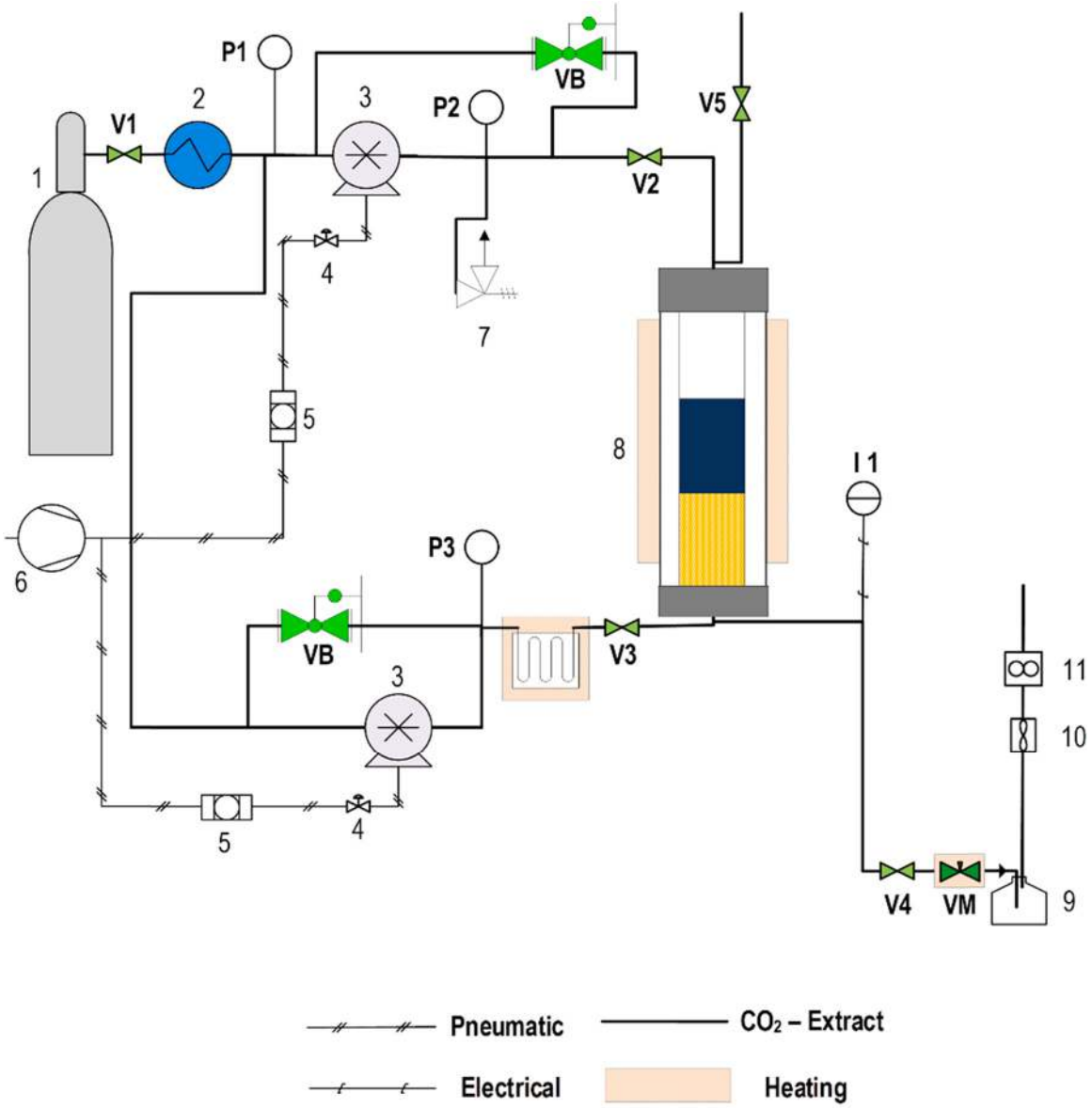
The samples before and after extraction by sCO_2 + MCP were analyzed in a scanning electron microscope at 15 kV and 100 pA (LEO Electron Microscopy/Oxford, Leo 440i) at the Laboratory of Analytical Resources and Calibration/UNICAMP, Campinas, Brazil. Before analysis, the humidity of the samples was conditioned as described in Section 2.3.

2.6. Prototype setup and operation mode of the sCO_2 + MCP process

This study proposed, for the first time, an apparatus that press and extracts at the same time. A schematic diagram of this unit, which is called sCO_2 + MCP unit, is shown in Figs. 1 and 2. For this purpose, we adopted the SFE-0.1L extraction unit in our previous study [27] as follows. A stainless-steel mobile piston with a diameter of 19.8 mm and a height of 28.2 mm is installed inside the extractor. This mobile piston divides the extractor into two parts: the lower part of the extractor contains raw-material and CO_2 at pressure of P_E, while the upper part of the extractor contains only CO_2 at pressure of P_P to apply the mechanical pressure on the raw material. These two parts are completely separated and were pressurized by two high pressure pumps. Other components of the unit are: CO_2 reservoir, cooling bath, control air pressure, air filter, air compressor, safety valve, extract collecting vessel, flowmeter, flow totalizer, temperature indicator, pressure gauge, blocking valve, micrometering valve, and back pressure valve. The technical characteristics of the components of this prototype are the same as those used in the SFE-0.1L extraction unit assembled in a previous study [27].

2.7. Experimental conditions

In a typical experiment, the raw material is fed to the extraction vessel, and the mobile piston is pushed down using a stainless-steel iron bar until the piston comes into contact with the raw material. Then, the extraction vessel is closed by placing the upper lid. After that, the valve V2 was opened to feed CO_2 to the upper part of the extraction vessel that does not contain any raw material. Immediately, valve V3 in Fig. 1 was opened to feed CO_2 to the lower part of the extraction vessel that contains the raw-material. The valves V2 and V3 were conveniently



1	CO_2 reservoir	9	Extract collecting vessel
2	Cooling bath	10	Flowmeter
3	Air-driven CO_2 pump	11	Flow totalizer
4	Control (air pressure)	I1	Temperature indicator
5	Air filter	P1 - P2 - P3	Pressure gauge
6	Air compressor	V(1, 2, 3, 4, 5)	Blocking valve
7	Safety valve	VM	Micrometering valve
8	Extraction vessel	VB	Back pressure valve

Fig. 1. Schematic diagram for sCO_2 + MCP.

manipulated to maintain a pressure differential (ΔP) of approximately 0.5 MPa until the pressure in the entire equipment becomes equal to the pressure of the CO_2 cylinder. Next, the pressurization of the upper and lower parts of the extractor begins to the desired pressures. Then, the system is kept under these conditions for 5 min (static time). The temperature was kept constant at 318 K based on our previous study [24].

In the design of experiments, two levels were considered for the piston pressure (P_P), i.e., 15 and 25 MPa. Piston pressure is the pressure in the upper part of the extraction vessel. For each value of P_P, the

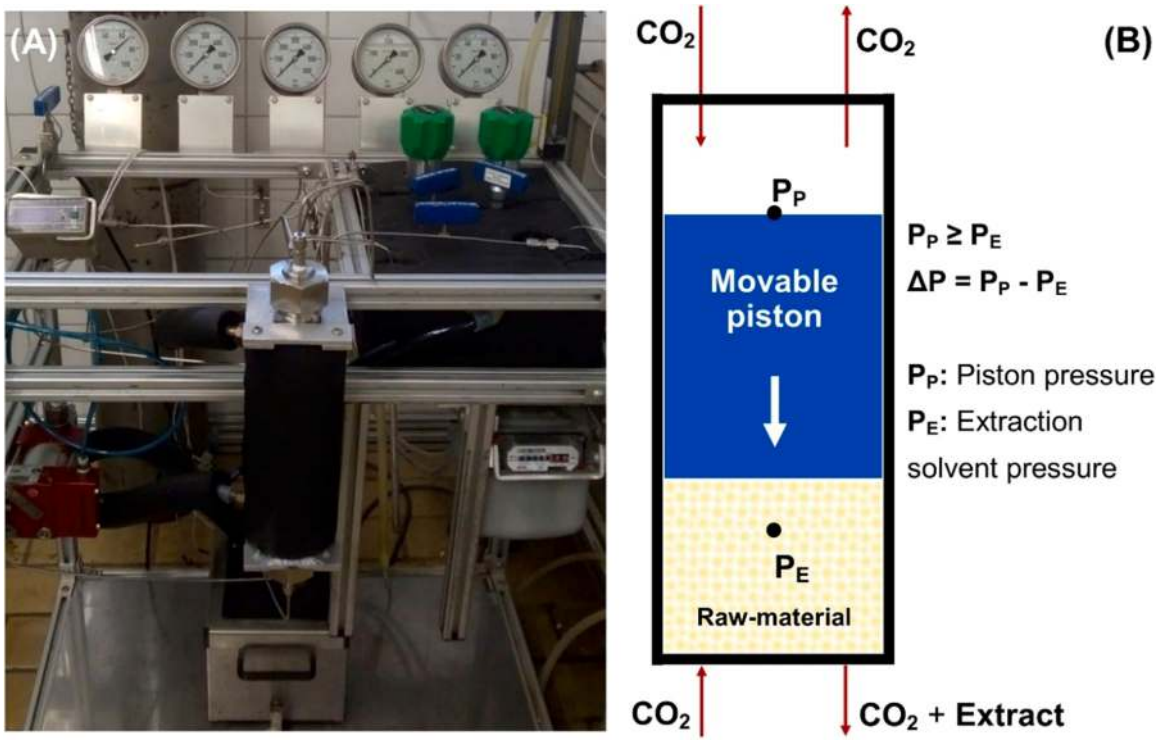


Fig. 2. A real image of the sCO_2 + MCP equipment (A) and a schematic graph of the extractor in the simultaneous extraction process (B).

extraction pressure (P_E), which is the pressure in the lower part of the extraction vessel where the raw material is located, was set to 10 MPa for the first experiment, and then it was increased by 5 MPa intervals for the next experiments until the P_P and P_E are approximately equal ($\Delta P \sim 0.5$ MPa). Therefore, for a P_P of 15 MPa, the P_E of 10 and 15 MPa was used, while for a P_P of 25 MPa, the P_E of 10, 15, 20, and 25 MPa was used. Each extraction was carried out using a 1.0×10^{-2} kg sample, a dynamic extraction time of 20 min and a mass flow of the solvent of 1.2×10^{-4} kg/s. All extraction assays were carried out in duplicate. The extraction yield (y, %) was calculated using the following equation:

$$y(\%) = \frac{m_{oil}}{m_{RM}} \times 100 \quad (2)$$

where m_{oil} is the mass of oil obtained (g) and m_{RM} is the mass of the raw material used in the extraction (g).

According to how the prototype works, the extraction bed is subjected to constant mechanical pressure during the supercritical extraction process, compacting the extraction bed to different degrees depending on the ΔP. Therefore, the height of the bed was determined in each extraction condition using a digital vernier (MTX 150 mm/6″, PROVELAB, Brazil) to examine the effect of mechanical pressure on the compaction of the bed.

2.8. Extraction kinetics

The kinetic experiments' operating conditions were the same as in the initial extractions (Section 2.6), concerning solvent flow, sample quantity, extraction temperature, and static time. Extract samples were collected at regular intervals until the oil content entirely of the sample was extracted. The extractions were carried out in duplicate to ensure the data's reliability. Additionally, the height of the extraction bed was determined before and after each extraction, as explained in Section 2.7.

3. Results and discussion

3.1. Sample characterization

The mean diameter of the BS particles after grinding was 1.8 ± 0.01 mm. It presented a humidity of $6.9 \pm 0.1\%$ (w/w); this value is within the range reported in the literature for in natura seeds with slight variations, which is probably due to the edaphoclimatic conditions of the place of production [28]. The content of ether extract or total oil was $24 \pm 2\%$ (w/w), this value is similar to that reported by Santos et al. [17], although other authors reported higher values (39.7–43.7% w/w) [29]; this can also be attributed to the fact that the fruits come from different production areas [29].

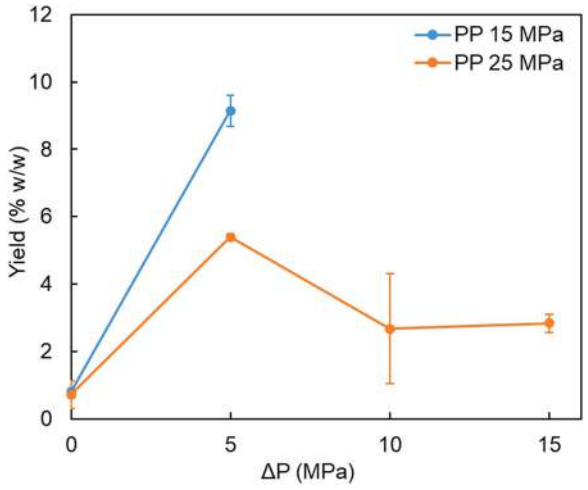


Fig. 3. Extraction yield at different ΔP from 0 to 15 MPa at the temperature of 318 K, S/F of 15.02 (kg/kg), and solvent flow rate of 1.2×10^{-4} kg/s.

3.2. Effect of P_P and P_E on overall yield

Fig. 3 shows the effect of the application of two piston pressure combined with different extraction pressure. In the case of P_P at 15 MPa, two P_E were applied, 10 and 15 MPa, which are corresponding to ΔP of 5 and 0 MPa, respectively. From these operating conditions, the highest yield (9.1% w/w) was obtained with a ΔP of 5 MPa. On the other hand, a P_P of 25 MPa was used with different P_E of 10, 15, 20 and 25 MPa, which are corresponding to the ΔP of 15, 10, 5 and 0, respectively. From these operating conditions, the highest yield (5.4% w/w) was again obtained with the ΔP of 5 MPa, followed by ΔP of 10 and 15 MPa, while the lowest yield was obtained with a ΔP of 0 MPa. In fact, the extraction yield increases from 2.8% to 5.4% w/w as ΔP decrease from 15 to 5 MPa, reaching the peak at 5 MPa, and decreases to 0.7% w/w at the ΔP of 0 MPa.

The higher extraction yield at the ΔP of 5 MPa compared to that of 0 MPa is due to the direct role of cold pressing in liberating more oil from particles, while the lower extraction yield at the ΔP of 10 and 15 MPa compared to that of 5 MPa is due to the excessive compaction of the bed that hinders the diffusion of sCO_2 towards the analyte of interest [18,19]. These results are in line with those obtained in our previous studies. It was found that the yield increased considerably when we applied a mechanical pressure prior to the SFE from the BS [24]. In another study, it was observed that the pressure applied by a torque of 40 Nm was the most adequate for SFEAP from fennel seeds, and an increase the torque up to 70 Nm did not improve the extraction yield [19]. A similar effect was observed in the SFEAP from clove buds when the torque was increased from 40 to 80 N m [18].

From the extraction results shown in Fig. 3, a sensitivity analysis can be performed based on the variation of ΔP (0–15 MPa) while keeping the P_E constant at 10 and 15 MPa. This analysis is represented in Fig. 4. The extractions shown in Figs. 3 and 4 were executed for a period of 20 min to initially evaluate the behavior of the overall extraction yield as a function of the variation in ΔP. It can be interpreted from Fig. 4 that the extraction yield, at P_E of 15 MPa, increases from 0.8% to 2.7% w/w as the ΔP increases from 0 to 10 MPa. At P_E of 10 MPa, the decrease in ΔP from 15 to 5 MPa leads to an increase in the extraction yield from 2.8% to 9.1% w/w. In addition, Fig. 5 compares the extraction yield obtained by different P_E (10, 20, and 30 MPa) at a constant ΔP of 5 MPa (which was the one that presented the highest overall extraction yield) after 8.33×10^{-1} h of extraction. The highest yield was obtained with an P_E of 10 MPa (13.9% w/w), followed by an P_E of 30 MPa (11.6% w/w) and 20 MPa (10.6% w/w). These results show that a combination of ΔP of 5 MPa and P_E of 10 MPa is the best extraction conditions for Baru oil.

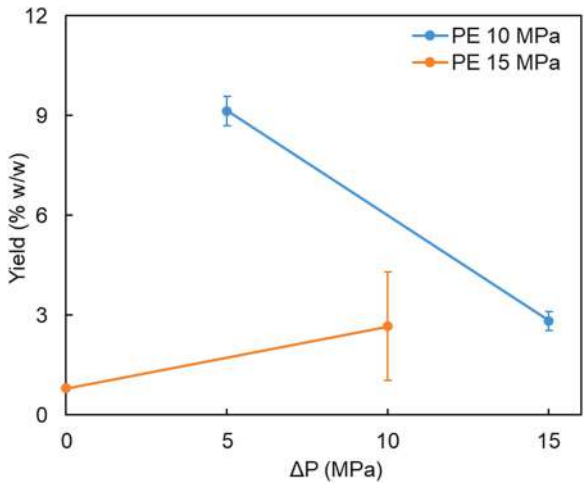


Fig. 4. Effect of ΔP (0–15 MPa) and extraction pressure (10 and 15 MPa) on the extraction yield at the temperature of 318 K, S/F of 15.02 (kg/kg), and solvent flow rate of 1.2×10^{-4} kg/s.

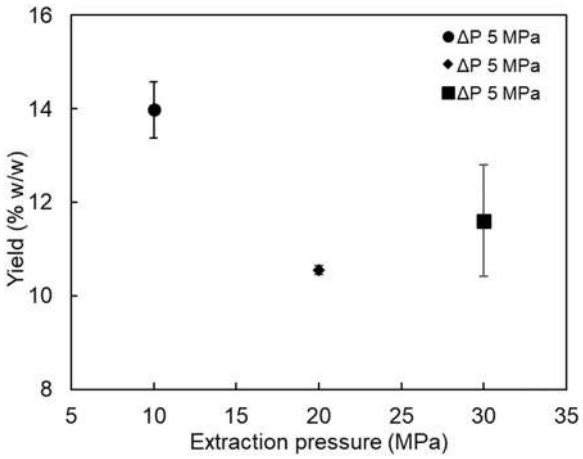


Fig. 5. The impact of P_E on the extraction yield at ΔP of 5 MPa, temperature of 318 K, extraction time of 8.33×10^{-1} h, and solvent flow rate of 1.2×10^{-4} kg/s.

Our results are similar to those obtained in the Gas-Assisted Mechanical Expression (GAME) process to recover oil rich in polyphenols from grape seeds [30]. The effective pressure in that study was calculated by subtracting the mechanical pressure minus the pressure of sCO_2, which is equivalent to ΔP in our study. Unlike the sCO_2 + MCP process, GAME requires much higher mechanical pressures and higher temperatures. They observed that the best effective pressure was 6.8 MPa with an extraction pressure of 53 MPa at 377 K [30]. These conditions, however, could not be used for the extraction of Baru oil mainly due to the high temperature that degrades the bioactive components [31]. Therefore, the main superiority of sCO_2 + MCP over GAME process is its capability to extract bioactive extracts using pleasant temperatures and lower pressures.

3.3. Effect of P_E and P_P on the physical characteristics of the extraction bed

Conventional SFE could change the physical structure of the bed due to the extraction of the analyte from the cells of the particles [32]; one of these physical alterations is shrinkage of seed particles that is the main assumption in the shrinking core model [33,34]. Although the porosity of the bed (ε_{bed}), in most models applied to pure SFE, is assumed constant until the end of the process [35], this assumption is not reliable for the SFE process combined with cold pressing. The effect of pressing on the porosity of the bed has not been reported in the SFEAP studies carried out with fennel [19], pequi [20], baru [24], and clove buds [18]. Just, a comparison was made with SFE in the fennel oil fractionation by SFEAP, observing that the application of cold pressing led to a dramatic drop in bed porosity, from 0.41 to 0.13 [19]. In the current study, we monitor

Table 1
Characterization of the extraction bed before and after extraction by sCO_2 + MCP.

Sample	Apparent density (kg/m^3)	Real density (kg/m^3)	Porosity (ε)
Before extraction in the vessel extraction	663.28	1179.1 ± 0.2	0.437
After extraction: P_P: 15 MPa/P_E: 10 MPa	1119.21	1207.7 ± 0.2	0.073
After extraction: P_P: 25 MPa/P_E: 20 MPa	1112.35	1210.9 ± 0.1	0.081
After extraction: P_P: 35 MPa/P_E: 30 MPa	1075.21	1203.7 ± 0.1	0.107

P_P: Piston pressure and P_E: Extraction pressure.

the porosity in all operating conditions, as shown in Table 1.

Although the ΔP is constant (5 MPa) in the three extraction conditions shown in Table 1, their corresponding porosities are different; the highest porosity is observed when we used P_P: 35 MPa/P_E: 30 MPa ($\varepsilon = 0.107$), followed by the conditions P_P: 25 MPa/P_E: 20 MPa ($\varepsilon = 0.081$), and P_P:15 MPa/P_E: 10 MPa ($\varepsilon = 0.073$). Fig. 6 shows SEM images of the extraction bed particles before and after the extraction process by sCO_2 + MCP. The compaction of the bed after the extraction process is evident by the presence of compact crusts of the raw material of the bed, as visualized in the condition ΔP: 5 MPa/P_E: 10 MPa, ΔP: 5 MPa/P_E: 20 MPa, and ΔP: 5 MPa/P_E: 30 MPa.

Bed compaction also affects the height of the extraction bed. Fig. 7 represents the heights of the bed before and after extraction for different operating conditions. Based on this figure, the initial height of the bed was 4.8×10^{-2} m, and the height of the bed after extraction for those with ΔP = 0 MPa is higher than those with ΔP > 0 MPa. Another point that can be drawn from this figure is that the high of the bed decreased considerably at the initial period of pressing, but it remains almost unchanged for the rest period of pressing. For example, in the extraction condition P_P: 15 MPa/P_E: 10 MPa, the height of the bed decreased significantly to 2.4×10^{-2} m at 20 min, and it stabilize to 2.3×10^{-2} m at 4.17 h. For the extraction condition of P_P: 25 MPa/P_E: 20 MPa, the height of the bed decreased considerably to 2.6×10^{-2} m at 20 min of extraction, and it drops slightly to 2.3×10^{-2} m at 4.17 h.

The results of porosity in Table 1 and bed height in Fig. 7 are directly connected. For example, the slightly smaller bed height in the case B compared to that of the case F, which both have the same extraction time of 20 min, can be justified by the slightly smaller porosity in the case B, 0.073, in comparison of the case F, 0.081. In addition, the bed height of the cases B* and F* are smaller than that of the cases B and F,

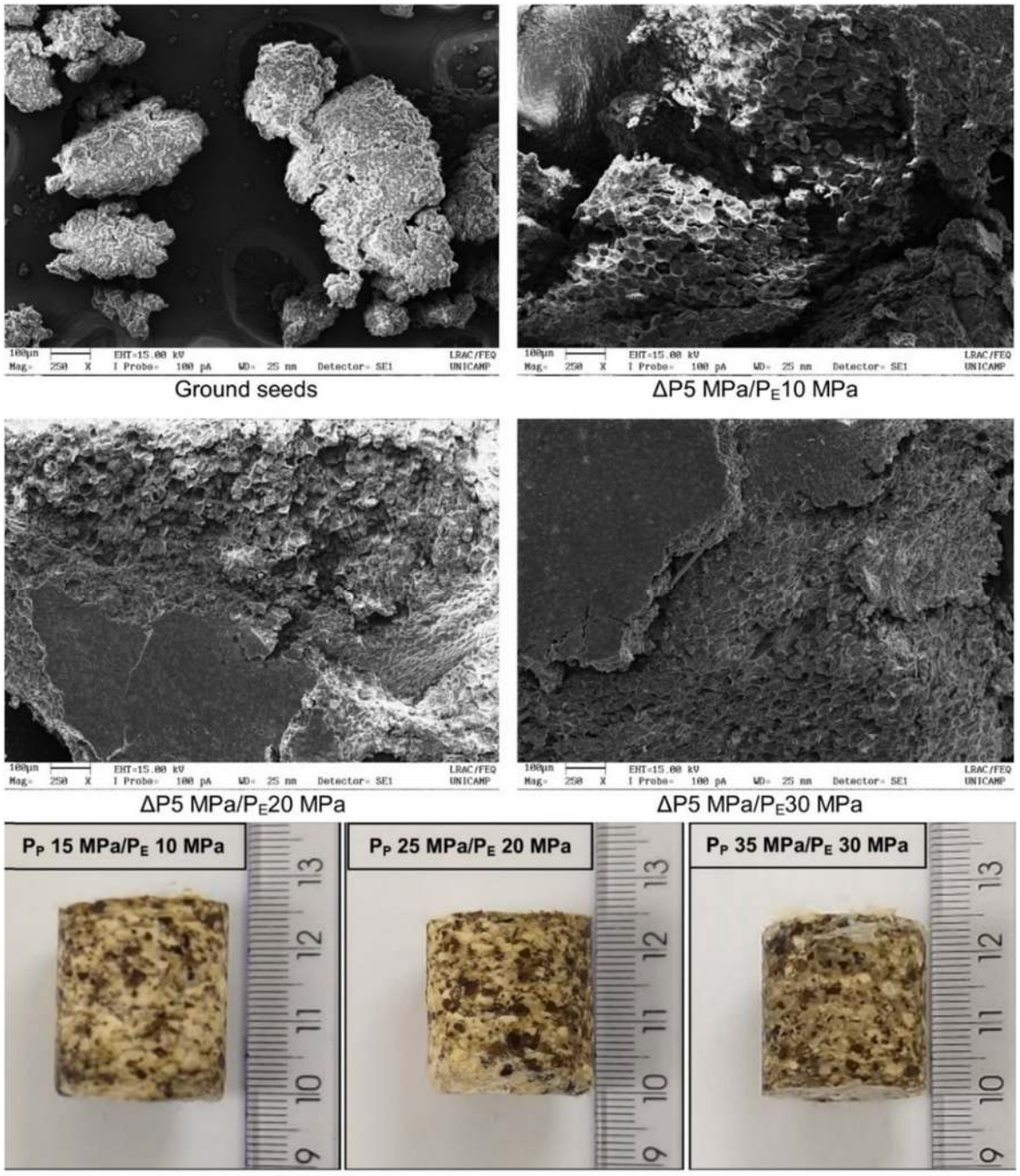


Fig. 6. SEM of the ground seeds particle after and before the sCO_2 + MCP process, and bed heights after extraction.

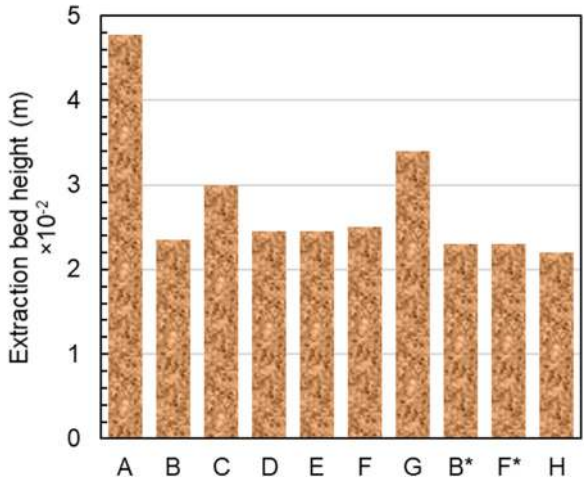


Fig. 7. Bed height before and after sCO_2 + MCP extraction process. Before extraction: A; After 20 min of extraction: B (ΔP 5 MPa/PE 10 MPa), C (ΔP 0 MPa/PE 15 MPa), D (ΔP 15 MPa/PE 10 MPa), E (ΔP 10 MPa/PE 15 MPa), F (ΔP 5 MPa/PE 20 MPa), G (ΔP 0 MPa/PE 25 MPa); and After 4.17 h of extraction: B*, F*, and H (ΔP 5 MPa/PE 30 MPa).

respectively, because of the higher extraction time in cases B* and F*, 4.17 h, that leads to higher oil depletion and smaller bed height.

3.4. Extraction kinetics

In the experimental extraction assays at different ΔP, it was observed that a ΔP equal to 5 MPa is the most suitable for obtaining bioactive extracts from BS. Accordingly, the extraction kinetics were constructed using this condition but with different values of P_P and P_E. Therefore, we worked with the following conditions: P_P: 15 MPa/P_E: 10 MPa, P_P: 25 MPa/P_E: 20 MPa and P_P: 35 MPa/P_E: 30 MPa; in these three conditions, the ΔP was remained constant at 5 MPa. The kinetics under these conditions were carried out until depletion of the bed extract (1.0×10^{-2} kg of ground BS), consuming a total time of 4.17 h (Fig. 8). It was found that the operating condition of P_P: 15 MPa/P_E: 10 MPa gives the highest extraction yield, followed by the condition with a P_P: 35 MPa/P_E: 30 MPa and P_P: 25 MPa/P_E: 20 MPa, obtaining final overall yields of 25.1%, 24.5% and 22.3% w/w, respectively. The two highest yields are similar to the value determined by Soxhlet (24% w/w). Therefore, the sCO_2 + MCP process is as efficient as the Soxhlet method for extraction from Baru oil, but with the advantage that it operates under lower P_E than that reported in the literature: 21.9% w/w obtained at 35 MPa and 45 °C by SFE [24], 22.6–22.8% w/w obtained at 35 MPa and 40–50 °C by SFE [17], and 28.6% w/w obtained at 35 MPa and 45 °C by SFEAP [24].

In the SFE extraction of oleaginous raw materials, in general, the extraction yield increases as the pressure increases, which was reported in the SFE from Aguaje pulp [4], *D. alata* seeds [17,24], macauba kernel [36], *Virola surinamensis* [3], and *Oenocarpus vacaba* [37]. In the current study, however, all the experimental points with ΔP of 5 MPa and P_E of 10 MPa are located above those with the P_E of 30 and 20 MPa at the same ΔP (Fig. 8).

4. Conclusion

A new extraction unit for simultaneous supercritical fluid extraction and cold pressing was successfully designed, built, and evaluated for obtained oil from BS. Simultaneous pressing and extraction significantly reduce the extraction pressure compared to the extraction without pressing and the extraction after pressing. The new sCO_2 + MCP process can achieve an even higher yield using a lower PE. A ΔP of 5 MPa, corresponding to a PP of 15 MPa and a PE of 10 MPa, had the highest extraction yield (25.1% w/w). The results show a new perspective for the supercritical extraction applied to oleaginous raw materials mainly due to the lower temperatures and pressures compared to the SFE process. More studies are still required on both the application of sCO_2 + MCP on other oilseeds and its scaling-up feasibility for industrial process.

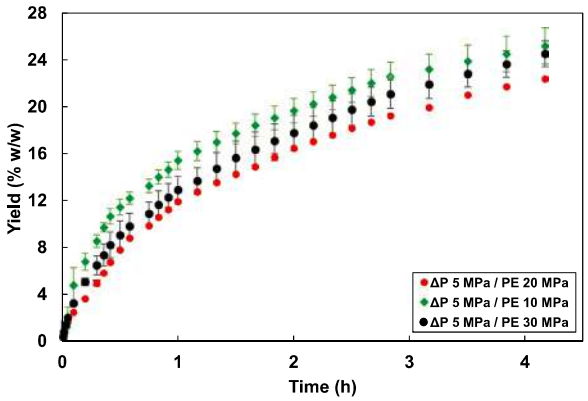


Fig. 8. Kinetics of the overall extraction yield at 10, 20, and 30 MPa. Under constant conditions: ΔP of 5 MPa, 318 K, and solvent flow rate of 1.2×10^{-4} kg/s.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CAPÍTULO V: *Discussões Gerais*

O estudo do comportamento do rendimento global de extração, composição e a avaliação econômica do processo de extração supercrítica da polpa de buriti, sementes de sucupira e baru, não estavam disponíveis na literatura atual. A extração de óleo da polpa de buriti a diferentes condições de pressão e temperatura, mostrou que o incremento destes dois parâmetros permite aumentar o rendimento global de extração. O perfil de ácidos graxos não variou com as condições de extração e foi identificado a presença de compostos bioativos da família dos terpenos. A qualidade do óleo de buriti extraído com dióxido de carbono supercrítico apresenta-se como uma alternativa interessante para a produção de alimentos funcionais e cosméticos.

A extração do óleo das sementes de sucupira com dióxido de carbono supercrítico teve um maior rendimento do que as condições subcríticas relatadas na literatura. O óleo obtido teve um perfil de composição de bioativos variável dependendo da condição de extração. Os maiores constituintes do óleo de sucupira foram o beta-cariofileno e alfa-humuleno, ambos com importante aplicações na indústria farmacologia e cosmética. A avaliação econômica do processo de extração supercrítica das sementes de sucupira é economicamente viável quando a extração é projetada para recuperar 27 g de óleo/100 g SB. Plantas de processamento com unidades de extração de duas colunas mostram uma melhor produtividade e menor custo de manufatura (COM) em comparação a unidades de extração com uma coluna de extração. As unidades de extração com duas colunas de extração permitem extrações paralelas ou consecutivas, esta última opção permite otimizar o tempo do processo melhorando a produtividade da planta.

O rendimento de óleo das sementes de baru variou dependendo do método de extração, o SFEAP permitiu incrementar o rendimento em comparação com o SFE, nas mesmas condições de temperatura e pressão. A qualidade do óleo em termos da presença de bioativos foi testada por cromatografia de camada delgada, observando-se a presença de compostos da família dos terpenos. O SFEAP incrementou as taxas de extração nos períodos CER e FER da curva global de extração. Como descrito na literatura a pressão mecânica contribuiu na liberação de extrato, incrementando as taxas de extração nesses dois períodos de extração. A avaliação econômica dos processos SFE e SFEAP, mostrou que o incremento da temperatura e pressão de extração, incrementa a produtividade do óleo e diminui o COM. O processo SFEAP apresentou um COM mais baixo do que o SFE, na melhor condição de extração (350 bar e 45ºC), esse efeito se deve ao maior rendimento de extração obtido com o SFEAP.

No método SFEAP, a prensagem mecânica e a extração SFE são executadas sequencialmente. Isto constitui uma desvantagem, porque se traduz em um aumento do tempo de operação, perdas de extrato na desmontagem do dispositivo de prensagem e exposição do extrato ao meio ambiente. As desvantagens mencionadas podem influir na qualidade dos extratos e no custo de produção. O novo método desenvolvido pretende diminuir essas desvantagens e possibilitar a sua aplicação a maior escala. A extração simultânea de bioativos utilizando a prensagem mecânica e a extração supercrítica foi denominada sCO_2+MCP. A aplicação deste novo método na extração de óleo de Baru permitiu diminuir a pressão de extração utilizando a prensagem mecânica simultânea, em comparação aos métodos SFE e SFEAP, um diferencial de pressão (prensagem mecânica – pressão do solvente de extração) de 5 MPa foi o mais adequado. A pressão de extração mais adequada para extração de óleo de Baru, reportada na literatura para os métodos SFE e SFEAP, é igual o próximo a 35 MPa para diferentes temperaturas. No novo método a pressão de extração mais adequada caiu até 10 MPa para uma boa recuperação de óleo das sementes de baru. Em termos gerais o método sCO_2+MCP é mais adequado para a recuperação de bioativos de alto valor biológico. Um processo de extração próximo ao desenvolvido neste presente estudo denominado GAME foi construído para a recuperação de óleo de sementes de uva. A diferença do GAME, o nosso processo sCO_2+MCP não utiliza um outro fluido como líquido hidráulico, a pressão mecânica é gerada pelo mesmo fluido supercrítico através de um dispositivo móvel (pistão) e a temperatura de operação pode ser graduada visando proteger os compostos termosensíveis.

CAPÍTULO VI: *Conclusões Gerais*

A extração supercrítica com CO_2 da polpa de buriti (MF), sementes de sucupira (PE) e baru (DA), foi realizada com sucesso. As melhores condições de extração permitiram obter rendimentos de 51,5 g óleo/100 g MF (40 MPa e 60 ºC), 40 g óleo/100 g PE (30 MPa e 40 ºC) e 21,9 g óleo/100 g DA (35 MPa e 45 ºC), para as três matérias-primas. O modelo *Spline* de três linhas retas descreve adequadamente o comportamento da cinética de extração das três matérias-primas. A composição de ácidos graxos do buriti não varia por efeito das condições de extração. O óleo de baru e buriti são ricos em ácidos graxos insaturados. O óleo de sucupira obtido na melhor condição de extração apresenta um maior número de compostos bioativos identificados por CG-MS. Adicionalmente, a avaliação econômica do processo de extração do óleo de sucupira por SFE, mostra que unidades de extração com duas colunas de 15 litros apresentam melhores indicadores econômicos do que unidades com uma coluna de extração de 30 litros.

Na extração de óleo das sementes de baru, o método SFEAP resultou ser mais eficiente do que o método SFE, obtendo-se um rendimento de extração global de 28,6 g óleo/100 g DA. A condição de extração que teve maior rendimento para ambos métodos foi a mesma, 35 MPa e 45 ºC. A modelagem matemática das cinéticas de extração para ambos métodos, com o modelo *Spline*, mostrou que a aplicação da prensagem mecânica incrementa as taxas de transferências de massa, nos períodos CER e FER. Isto aconteceu provavelmente pela maior disponibilidade do analito para saturar o CO_2, provindas das células quebradas pela prensagem mecânica no método SFEAP. A composição de ácidos graxos não foi afetada pela aplicação dos dois métodos, mas foi observado pequenas variações na concentração por efeito da pressão e temperatura de extração. O óleo de baru obtido por ambos métodos mostrou a presença de compostos da família dos terpenos. Uma avaliação econômica comparativa dos dois métodos para a obtenção do óleo de baru, mostrou que o SFEAP apresenta melhor produtividade e menor custo de manufatura.

A unidade sCO_2+PMF foi desenhado e construído com sucesso. Este novo processo foi aplicado a extração de sementes de Baru e os resultados comparados com os métodos SFE e SFEAP. Os resultados mostram que a unidade sCO_2+PMF permite reduzir a pressão de extração dos métodos SFE e SFEAP, obtendo-se rendimentos de extração semelhantes de óleo de Baru. Uma diferença de pressão de 5 MPa, entre a pressão mecânica (15 MPa) e a pressão de extração (10 MPa) foi a melhor para a matéria-prima estudada, obtendo-se um rendimento total de 25%. Os resultados do estudo sugerem uma perspectiva interessante para a aplicação do novo método em matérias-primas com alto teor de lipídios,

consequentemente, mais estudos são necessários para avaliar novas matérias-primas, scale-up e o efeito das condições de extração na composição de bioativos.

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ANEXOS

Anexo 1:

MEMORIA DO PERÍODO DE DOUTORADO

O doutorando Larry Oscar Chañi Paucar ingressou no programa de pós-graduação de Engenharia de Alimentos da Unicamp em 2019 através do processo seletivo do Departamento de Engenharia de Alimentos (DEA), contando com uma bolsa da CAPES (Codigo 001). O doutorando cursou cuatro disciplinas obrigatórias: TP-320 Termodinâmica; TP-322 Fenômenos de Transporte I; TP-323 Fenômenos de Transporte II; TP-199 Seminários e dois disciplinas optativas oferecidas no respectivo departamento: TP-159 Tópicos Especiais em Engenharia de Alimentos; e TP-121 Tópicos em Engenharia de Alimentos, totalizando 17 créditos.

Produção científica:

1. Artigo: **Supercritical Fluid Extraction from Aguaje (*Mauritia flexuosa*) Pulp: Overall Yield, Kinetic, Fatty Acid Profile, and Qualitative Phytochemical Profile**, publicado em The Open Food Science Journal, https://doi.org/10.2174/1874256402113010001

2. Artigo: **Technical and economic evaluation of supercritical CO_2 extraction of oil from sucupira branca seeds**, publicado no periodico The Journal of Supercritical Fluids. https://doi.org/10.1016/j.supflu.2021.105494

3. Artigo: **A comparative and economic study of the extraction of oil from Baru (*Dipteryx alata*) seeds by supercritical CO_2 with and without mechanical pressing**, publicado em Heliyon, https://doi.org/10.1016/j.heliyon.2021.e05971

4. Artigo: **Simultaneous integration of supercritical fluid extraction and mechanical cold pressing for the extraction from Baru seed**, publicado no periodico The Journal of Supercritical Fluids, https://doi.org/10.1016/j.supflu.2022.105553

5. Capítulo de livro: **Extraction of polyphenols by sub/supercritical based technologies**, submetido para publicar no livro: Technologies to Recover Polyphenols from AgroFood By-products and Wastes, pela Elsevier Publisher.

6. Capítulo de livro: **Supercritical Fluid Extraction**, submetido para publicar no livro: Green Extraction Techniques in Food Analysis, E-book Series "Food Science: Current and Future Developments", pela Bentham Science.

7. Resumo: **Supercritical fluids extraction assisted by pressing from baru (*Dipteryx alata*) seeds**, apresentado na forma de pôster no V Iberoamerican Conference on Supercritical Fluids, https://www.prosciba.fea.unicamp.br/?q=node/18

8. Resumo: **Supercritical fractionation of baru seed oil**, apresentado na forma de pôster no V Iberoamerican Conference on Supercritical Fluids, https://www.prosciba.fea.unicamp.br/?q=node/18

9. Resumo: **Phenolic compounds recovery from pomegranate (*Punica granatum*) agroindustrial waste using pressurized liquid extraction**, apresentado na forma de pôster no 3er Congreso Iberoamericano de Ingeniería de los Alimentos (CIIAL 2020), http://ciial.org.uy/ebook/

10. Resumo: **Simultaneous Extraction by Supercritical CO_2 and Cold Pressing**, apresentado na forma de pôster no 18 th European Meeting on Supercritical Fluids.

Anexo 2: Cadastro SisGen da especie *Dipteryx alata*

Ministério do Meio Ambiente
CONSELHO DE GESTÃO DO PATRIMÔNIO GENÉTICO

SISTEMA NACIONAL DE GESTÃO DO PATRIMÔNIO GENÉTICO E DO CONHECIMENTO TRADICIONAL ASSOCIADO

Comprovante de Cadastro de Acesso

Cadastro nº A2F3B9E

A atividade de acesso ao Patrimônio Genético, nos termos abaixo resumida, foi cadastrada no SisGen, em atendimento ao previsto na Lei nº 13.123/2015 e seus regulamentos.

Número do cadastro:	**A2F3B9E**
Usuário:	**Júlio Cezar Johner Flores**
CPF/CNPJ:	**024.193.121-55**
Objeto do Acesso:	**Patrimônio Genético**
Finalidade do Acesso:	**Pesquisa e Desenvolvimento Tecnológico**

Espécie

Dipteryx alata

Título da Atividade:	**Extraction of baru fruit**

Equipe

Júlio Cezar Johner Flores	**UNICAMP**
Larry Oscar Chañi Paucar	**UNICAMP**
Maria Angela de Almeida Meireles Petenate	**UNICAMP**

Parceiras Nacionais

46.068.425/0001-33 / Universidade Estadual de Campinas

Data do Cadastro:	**26/01/2019 17:18:37**
Situação do Cadastro:	**Concluído**

Conselho de Gestão do Patrimônio Genético
Situação cadastral conforme consulta ao SisGen em **17:23** de **26/01/2019**.

SISTEMA NACIONAL DE GESTÃO DO PATRIMÔNIO GENÉTICO E DO CONHECIMENTO TRADICIONAL ASSOCIADO - **SISGEN**

Anexo 3: Cadastro SisGen da especie *Pterodon emarginatus*

Ministério do Meio Ambiente
CONSELHO DE GESTÃO DO PATRIMÔNIO GENÉTICO

SISTEMA NACIONAL DE GESTÃO DO PATRIMÔNIO GENÉTICO E DO CONHECIMENTO TRADICIONAL ASSOCIADO

Comprovante de Cadastro de Acesso

Cadastro nº AD6F211

A atividade de acesso ao Patrimônio Genético, nos termos abaixo resumida, foi cadastrada no SisGen, em atendimento ao previsto na Lei nº 13.123/2015 e seus regulamentos.

Número do cadastro:	**AD6F211**
Usuário:	**UNICAMP**
CPF/CNPJ:	**46.068.425/0001-33**
Objeto do Acesso:	**Patrimônio Genético**
Finalidade do Acesso:	**Pesquisa e Desenvolvimento Tecnológico**

Espécie

Pterodon emarginatus

Título da Atividade:	**Extração com Fluido Supercrítico das sementes de Sucupira**

Equipe

Júlio Cezar Johner Flores	**UNICAMP**
Larry Oscar Chañi Paucar	**UNICAMP**
Maria Angela de Almeida Meireles Petenate	**UNICAMP**

Parceiras Nacionais

46.068.425/0001-33 / Universidade Estadual de Campinas

Data do Cadastro:	**26/01/2019 16:48:44**
Situação do Cadastro:	**Concluído**

Conselho de Gestão do Patrimônio Genético
Situação cadastral conforme consulta ao SisGen em **16:49** de **26/01/2019**.

SISTEMA NACIONAL DE GESTÃO DO PATRIMÔNIO GENÉTICO E DO CONHECIMENTO TRADICIONAL ASSOCIADO - **SISGEN**

Anexo 4:

Anexo 5:

Anexo 6: