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WANESSA ALMEIDA DA COSTA

EXTRAÇÃO E TRANSESTERIFICAÇÃO DO ÓLEO DE RESÍDUO INDUSTRIAL DE PALMISTE USANDO METANOL SUPERCRÍTICO

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Tese apresentada ao Programa de Pós-Graduação em Engenharia de Recursos Naturais da Amazônia da Universidade Federal do Pará como requisito parcial para a obtenção do grau de Doutora em Engenharia de Recursos Naturais da Amazônia

ORIENTADOR: Prof. Dr. Raul Nunes de Carvalho Junior

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"É muito melhor lançar-se em busca de conquistas grandiosas, mesmo expondo-se ao fracasso, do que alinhar-se com os pobres de espírito, que nem gozam muito nem sofrem muito, porque vivem numa penumbra cinzenta, onde não conhecem nem vitória, nem derrota."

Theodore Roosevelt

RESUMO

O palmiste é uma semente oleaginosa encontrada em frutos de *Elaeis guineensis* Jacq. e que representa um dos principais óleos consumidos no mundo, com uma produção média de 18,59 milhões de toneladas. Seu principal processo de obtenção é a extração por prensagem mecânica que gera, no mundo, aproximadamente 9,6 x 10^9 toneladas de resíduo também chamado de torta residual. Uma vez que esse resíduo pode ainda apresentar cerca de 12% de óleo remanescente, a extração por fluido supercrítico (EFS) é apresentada como uma alternativa à recuperação deste óleo. A extração por Soxhlet também foi feita para que fosse comparada com a EFS. Pressões de 150, 250 e 350 bar e temperaturas de 40, 60 e 80 °C foram utilizadas nos experimentos. A matéria-prima foi caracterizada antes e depois da EFS por umidade, cinzas, fibras, proteínas e lipídeos e os extratos foram caracterizados por cromatografia gasosa/espectrometria de massas (CG/EM). Os dados cinéticos foram comparados ao modelo de Sovová (2012) e a condição de maior rendimento foi usada nos experimentos de transesterificação. Foram usadas razões molares de 1:24 e 1:42 (óleo:metanol), temperaturas de 250, 300 e 350 °C, pressão constante de 200 bar e tempos reacionais de 5, 10, 15, 20 e 25 minutos. Os produtos também foram analisados por CG/EM para verificação da transformação dos triacilglicerois em ésteres metílicos. Os principais resultados deste estudo foram: a EFS não altera a composição centesimal da matéria-prima; a condição de maior rendimento foi 350 bar e 80 °C; o modelo de Sovová (2012) se ajustou bem aos dados cinéticos; a condição 1:42, 350 ºC foi a que obteve maior teor de ésteres (99,81%) em apenas 5 minutos de reação. A transesterificação de óleo de palmiste em meio supercrítico é uma alternativa válida e que apresenta vantagens em relação ao método convencional, entretanto uma análise mais aprofundada considerando as limitações técnicas e econômicas deste método é necessária.

Palavras-chave: Palmiste. Extração por fluido supercrítico. Torta residual. Transesterificação supercrítica. Biodiesel.

ABSTRACT

Palm kernel is an oleaginous seed found in fruits of *Elaeis guineensis* Jacq. and which represents one of the main oils consumed in the world, with an mean production of 18,59 million tons. Its main process is the extraction by mechanical pressing that generates, in the world, approximately 9.6 x 109 tons of residue also called residual cake. Since this residue can still present about 12% of remaining oil, supercritical fluid extraction (SFE) is presented as an alternative to the recovery of this oil. Soxhlet extraction was also performed to be compared to the SFE. Pressures of 150, 250 and 350 bar and temperatures of 40, 60 and 80 °C were used in the experiments. The raw material was characterized before and after the SFE by moisture, ash, fibers, proteins and lipids contents and the extracts were characterized by gas chromatography/mass spectrometry (GC/MS). The kinetic data were compared to the Sovová (2012) model and the condition of highest yield was used in the transesterification experiments. Molar ratios of 1:24 and 1:42 (oil: methanol), temperatures of 250, 300 and 350 °C, constant pressure of 200 bar and reaction times of 5, 10, 15, 20 and 25 minutes were used. The products were also analyzed by GC/MS to verify the transformation of triacylglycerols into methyl esters. The main results of this study were: SFE does not alter the centesimal composition of the raw material; the condition of highest yield was 350 bar and 80 °C; Sovová's model had the best fit to the kinetic data; the condition 1:42, 350 ºC was the one that obtained the highest content of esters (99.81%) in only 5 minutes of reaction. The transesterification of palm kernel oil in a supercritical medium is a valid alternative and presents advantages over the conventional method, however a more in-depth analysis considering the technical and economic limitations of this method is necessary.

Keywords: Palm kernel. Supercritical fluids extraction. Residual cake. Supercritical transesterification. Biodiesel.

SUMÁRIO

CAPÍTULO 1

1. INTRODUÇÃO GERAL

Os atuais programas e projetos de desenvolvimento para a Amazônia têm indicado a preocupação com a sustentabilidade sob os pontos de vista social, econômico e ambiental. O desafio está na promoção de um modelo de desenvolvimento rural aproveitando suas potencialidades, comprometendo o mínimo possível suas funções ambientais. Neste contexto, o Pará é o maior produtor de óleo de palma do Brasil, com atividades que correspondem a 95% da produção nacional, tendo várias empresas que o exploram industrialmente. Como exemplo pode-se citar a Agropalma S.A., que ocupa uma área total de 107 mil hectares, com fábricas de óleo bruto nos municípios de Tailândia, Moju, Acará e Tomé-Açu com capacidade de processar 320 toneladas de óleo bruto/dia, detendo 75% da produção nacional de óleo de palma (AGROPALMA, 2014; FIEPA, 2014).

Entretanto, o crescimento acelerado e expressivo do cultivo dessa palmácea pode contribuir para o aumento de subprodutos orgânicos e biomassa, oriundos tanto do campo quanto da usina. A partir do processamento dos frutos do dendezeiro há o fornecimento, em média, dos seguintes produtos: óleo de palma bruto, 20%; óleo de palmiste, 1,5% e os seguintes subprodutos: torta de palmiste, 3,5%; engaços, 22%; fibras, 12%; cascas, 5%; e efluentes líquidos, 50%. Gerando um total de aproximadamente 600.000 toneladas/ano de resíduos (BEZERRA et al., 2018; EMBRAPA, 2006).

Em relação à destinação dada a esses resíduos, a torta de palmiste, devido a seu alto valor energético, é muitas vezes utilizada como suplemento de ração animal (AKINYEYE et al., 2011) e uma forma de garantir a manutenção desses nutrientes é fazendo a re-extração do óleo residual presente através da tecnologia do fluido supercrítico, uma vez que nela não há uso de solventes orgânicos, o que prejudicaria seu uso por parte dos animais.

Desta forma, a utilização da biomassa da indústria do dendê, em especial a torta resultante da extração do óleo de palmiste, que ainda apresenta em sua composição até 12% de óleo residual, pode representar uma alternativa para a produção de combustíveis de origem fóssil, podendo ser empregado como fonte de energia renovável na matriz energética na forma de biodiesel, impulsionando o desenvolvimento econômico regional (BEZERRA et al., 2018; AB RAHMAN et al., 2012).

O biodiesel apresenta vantagens sobre os combustíveis de origem fóssil devido não apresentarem em sua composição enxofre e compostos aromáticos, possuir alto número de cetano, teor médio de oxigênio, maior ponto de fulgor, menor emissão de partículas (HC, CO e CO_2), baixa toxicidade, além de ser biodegradável (FERRARI et al., 2005; QUEIROZ et al., 2012; SANTANA, 2012). O método mais comum de produção de biodiesel é através da transesterificação que consiste em uma reação química que pode ou não ser catalisada, envolvendo um óleo (fonte de triglicerídeos) e um álcool para produzirem ésteres alquílicos de ácidos graxos (biodiesel) e glicerol (subproduto) (FALCÃO, 2011; GUI et al., 2009).

Este método, comumente empregado, utilizando catalisadores, pode conduzir a reações secundárias indesejáveis e a um menor rendimento de ésteres, devido à maior sensibilidade à presença de água e ácidos graxos livres, levando a passos de separação e purificação dispendiosos, necessários para remover produtos secundários (sabão e catalisadores que não reagiram). Por conseguinte, há um maior requerimento de energia para realizar a purificação e tratar das águas residuais geradas durante o processo (RODRÍGUEZ-GUERRERO et al., 2013; TAN, et al. 2010).

Neste panorama, uma alternativa viável para solucionar esta problemática é o emprego do álcool supercrítico para a realização da transesterificação. O álcool supercrítico, ou seja, com temperatura e pressão acima do ponto crítico, forma apenas uma fase com o óleo, ao invés de duas como em condição ambiente, fazendo com que haja uma redução na constante dielétrica do álcool no estado supercrítico (MICIC et al., 2014; SANTANA et al., 2012).

Vários estudos (HAN et al, 2005; BERTOLDI et al, 2009; IMAHARA et al., 2009; LIM e LEE, 2013; MAEDA et al., 2011) relatam que o emprego de um cossolvente adequado, como por exemplo o dióxido de carbono, pode influenciar no aumento da miscibilidade da interface entre o álcool e óleo no processo da transesterificação. As principais vantagens são de não haver a necessidade de uma etapa posterior de retirada do catalisador e produtos de saponificação e menor requisição de energia no processo global (KASTEREN e NISWORO, 2007). De acordo com o cenário apresentado, esta tese teve como objetivo geral obter o óleo do resíduo industrial de palmiste empregando a partir do dióxido de carbono supercrítico e utilizar este óleo na transesterificação com metanol supercrítico.

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1.1 OBJETIVOS DA PESQUISA

1.1.1 Objetivo Geral

- ✓ Transesterificar o óleo de resíduo industrial de palmiste com metanol supercrítico.

1.1.2 Objetivos Específicos

- ✓ Estudo sistemático da preparação e caracterização físico-química do resíduo de palmiste;
- ✓ Extrair óleo de resíduo de palmiste utilizando dióxido de carbono supercrítico em diferentes condições de temperatura, pressão e densidade;
- ✓ Extrair óleo de resíduo de palmiste por Soxhlet;
- ✓ Determinar o rendimento de cada um dos métodos;
- ✓ Determinar as isotermas de rendimento global da EFS;
- ✓ Determinar o perfil de ácidos graxos nos extratos obtidos pelos dois métodos;
- ✓ Determinar a cinética de extração do óleo de palmiste via ESF, verificando o modelo matemático que mais se adequa ao processo;
- ✓ Validar um reator semi-contínuo através de processo de transesterificação de óleo de soja com metanol e CO_2 supercrítico como catalisador e analisar seu produto quanto à conversão dos triacilglicerois em ésteres metílicos;
- ✓ Realizar a transesterificação de óleo de palmiste com metanol supercrítico, obtendo frações do produto da reação;
- ✓ Analisar as frações obtidas quanto à conversão dos triacilglicerois em ésteres metílicos.

CAPÍTULO 2

1. REVISÃO DA LITERATURA

Palmiste é uma semente oleaginosa encontrada em frutos de *Elaeis guineenses* Jacq., que é uma palmeira originária do continente africano, oriunda do Golfo da Guiné e encontrada no Senegal, Angola, Costa do Marfim, Camarões e Zaire. A planta também se adaptou às regiões tropicais com clima quente e úmido de outros países como Brasil, Indonésia, Malásia, Tailândia, entre outros (OLIVEIRA et al., 2015; OIL WORLD, 2016).

É conhecida popularmente como dendenzeiro, palma-de-guiné, dendem, palmeira dendem e coqueiro-de-dendê. A espécie é classificada cientificamente como pertencente ao reino Plantae, divisão Magnoliophyta, classe Liliopsida, ordem Arecales, família Arecaceae, subfamília Arcoideae, tribo Cocoseae, subtribo Elaeidina e gênero Elaeis (CORLEY, 1973).

O cultivo da *Elaeis guineensis* Jacq. é influenciado por alguns fatores climáticos como chuva, horas de luz solar e temperatura. A temperatura média de cultivo deve estar entre 24 e 32 ºC, sem ocorrer quedas de temperatura abaixo de 19 ºC por períodos prolongados, visto que a temperatura tem efeito sobre o número de folhas emitidas, número de cachos produzidos e teor de óleo nos frutos. As chuvas devem proporcionar precipitações mínimas anuais de 2000 mm e mensais de 100 mm, pois a disponibilidade de água determina produções elevadas de cachos de dendê. A incidência solar deve ser de 1.500 a 2.000 horas/luz/ano com mínimo de 5 horas/luz solar/dia e a umidade relativa do ar deve estar em torno de 80% (ALVARADO-VEGA e STERLING-RODRÍGUEZ, 1998; CORLEY e TINKER, 2016; SMITH, 1989).

Nesta espécie, o palmiste (amêndoa) começa a produzir óleo com aproximadamente 50 dias de antecedência em relação ao mesocarpo que inicia a sua produção com 120 dias a partir da formação do cacho, em cada fruto podem ser encontradas mais de uma amêndoa contida em cada semente, sendo mais comum que haja apenas uma amêndoa já que o seu sistema reprodutor ocasiona o aborto de dois óvulos nos casos de aparecimento de ovários tricarpelar, que nada mais são do que ovários com três embriões fecundados (Ver Figura 1) (BORGES et al., 2016).

Figura 1: Cacho de *E. guineensis* (A) e fruto da palma mostrando o mesocarpo (polpa) e o endosperma (amêndoa) (B). Adaptação de CAMILLO (2012).

A produção comercial deve iniciar após três anos de plantio, com uma estimativa de 6 a 8 toneladas de cachos/ha, sendo que no oitavo ano a produção deve alcançar o seu ápice com produção de 20 a 35 toneladas de cachos/ha, apresentando um décimo no sexto ano até fim da vida útil produtiva do dendezeiro aos 25 anos. O replantio é aconselhável quando cerca de 30% das árvores estão mortas ou já inacessíveis para colheita pela altura (12 a 13 m) (FIGUEREDO VARGAS, 1981; ZIMMER, 2016).

Historicamente, a demanda por sementes era muito superior à do óleo, devido ao seu alto consumo. Progressivamente, a exportação de sementes aumentou consideravelmente e por consequência, a demanda por óleo de palmiste, iniciando suas exportações por volta de 1832. A taxa de crescimento das exportações declinou algumas décadas após a segunda guerra mundial (CORNELIUS, 1977; CORLEY e TINKER, 2016).

Atualmente, o palmiste está entre as principais sementes oleaginosas do mundo, com produção estimada em 18,59 milhões de toneladas em 2017 (USDA, 2018). Seus principais produtores mundiais são Indonésia, Malásia, Tailândia, Nigéria e Colômbia, respectivamente, sendo a Colômbia e Tailândia os países que apresentam maior taxa de crescimento em suas produções (INDEX MUNDI, 2018).

Em relação ao óleo de palma, a produção de palmiste é de cerca de 10% da quantidade de óleo de palma, sendo suas características físicas e composições químicas muito diferentes, gerando possibilidades de aplicações diferentes (BERGER e NORAINI, 2005).

A cultura do palmiste tem uma representação socioeconômica importante para os países que o produzem. São cultivados tanto por pequenos produtores em fazendas familiares, como em plantações de grande escala (KUSUMANINGTYAS e GELDER, 2017). Esta cultura gera desafios para equilibrar o aumento de rendimentos com a redução do desmatamento de florestas tropicais para plantio e ainda redução de resíduos industriais de processos de extração de óleo (NORHAIZAN et. al., 2013; FITZHERBERT et.al., 2008; KOH e WILCOVE, 2008).

Atualmente, existem diversos métodos que vêm sendo utilizados no processo de obtenção de matérias graxas. O óleo de palmiste pode ser extraído, por exemplo, por extração mecânica, por solvente, microemulsão e por extração com fluido supercrítico (NORHAIZAN et. al., 2013). A produção desse óleo apresenta benefícios socioambientais, como: aumento na geração de emprego e renda e consequentemente melhora na qualidade de vida dos produtores, e desenvolvimento do comércio, com oferta de emprego (SARGEANT, 2001; BASIRON, 2007). Em relação aos avanços sobre a cultura e ainda, novas áreas de aplicações do palmiste, diversas alternativas vem sendo estudadas, desde melhorias no cultivo e novos métodos de obtenção do óleo, até a elaboração de novos produtos, como biocombustíveis, cosméticos e derivados alimentícios (CROS et al., 2015; SILVA e ENGELMANN, 2017; SILVA e BATALHA, 2013; BASHIR et.al., 2015).

Considerado um dos mais antigos métodos de obtenção de óleos e gorduras, a técnica mais utilizada para extração de óleo de palmiste é a prensagem mecânica. Este método baseia-se na alimentação, rotação, movimentação e compressão de sementes e frutos no interior da prensa de rosca. É formado por barras de aço e lâminas, cuja espessura depende do estoque (COSTA et al., 2017; RAMALHO e SUAREZ, 2013). Ver Figura 2.

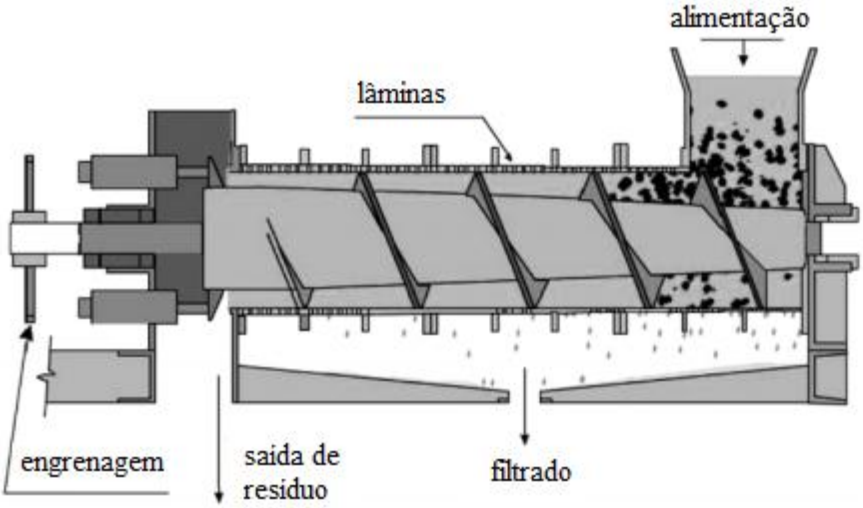


Figura 2. Seção transversal de uma prensa mecânica (IBRAHIM, 2013)

A extração de óleo de palmiste requer pré-tratamento, que pode incluir redução de tamanho, fissuração, secagem, peneiramento, pré-aquecimento, etc. Isso é necessário para extrair eficientemente o óleo dos grãos. Em primeiro lugar, eles devem ser limpos de materiais que possam contaminar os produtos e causar danos ao equipamento. A fim de remover resíduos de metal, pedras, areia e outros materiais indesejáveis, separadores magnéticos e peneiras vibratórias são comumente instalados (SAVOIRE et al., 2013; ROMBAUT et al., 2015; FIRDAUS et al., 2017).

A popularidade desta técnica reside na sua simplicidade, facilidade de manutenção e no fato de poder ser adaptada para o processamento de diferentes tipos de sementes oleaginosas. 86 a 92% do óleo podem ser obtidos, bem como um resíduo rico em proteína livre de produtos químicos (PRADHAN et al., 2011).

Outro método de extração de óleos é aquele que utiliza um solvente orgânico em seu processo. O Soxhlet, por exemplo, é uma técnica padrão e bem estabelecida que tem sido usada há muito tempo para extrações do tipo sólido-líquido (ver a figura 3).

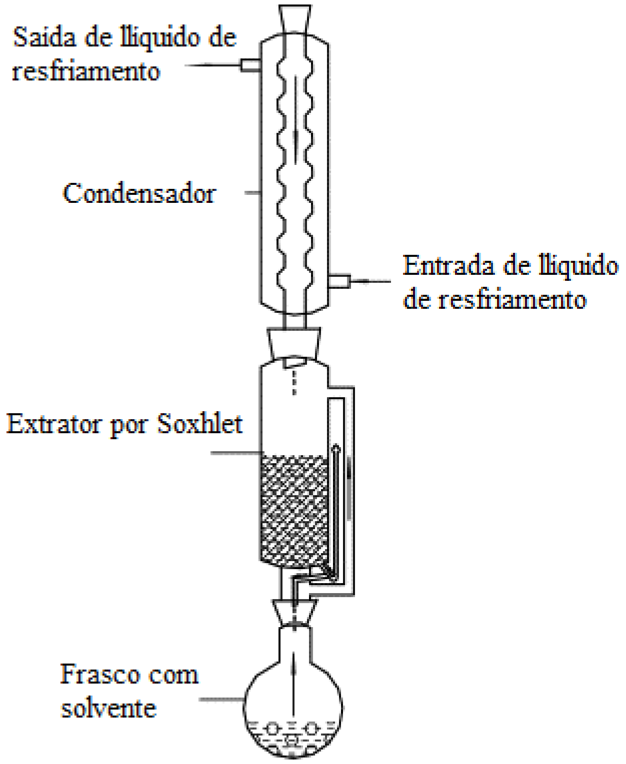


Figura 3. Aparelho de Soxhlet (WANG e WELLER, 2006)

Uma vez que um solvente orgânico é usado, a qualidade do produto pode reduzir por causa das vários etapas necessárias para recuperar o solvente, tais como temperatura elevada e extração de compostos indesejáveis (WANG e WELLER, 2006; RIBEIRO et al., 2012). Alguns solventes usados nesta técnica são hexano, n-hexano, pentano, etanol e éter de petróleo (DANLAMI et al., 2015; TODA et al., 2016). As principais vantagens deste tipo de extração são: procedimento simples e barato, uma temperatura de extração relativamente alta e nenhuma filtragem é necessária após o processo. Por outro lado, as principais desvantagens incluem: longo tempo de extração, uso de uma grande quantidade de solvente e a possibilidade de decomposição térmica das substâncias desejadas (WANG e WELLER, 2006).

Para a recuperação do óleo existente no resíduo da prensagem industrial, a técnica de extração por fluido supercrítico (EFS) vem sendo empregada. Um fluido que coexiste em uma condição acima de sua temperatura (Tc) e pressão críticas (Pc) pode ser definido como no estado supercrítico. Fluidos supercríticos são intermediários entre líquidos e gases. Portanto, características físico-químicas como densidade, viscosidade e difusividade são facilmente alteradas pela temperatura e pressão (SAHENA et al., 2009; AKANDA et al., 2012).

A EFS pode ser considerada uma alternativa aos processos convencionais de extração e refino de óleo. As principais vantagens desta técnica incluem operação a baixa temperatura, alta seletividade, recuperação de componentes valiosos e também é considerado um mecanismo verde (HONG et al., 2010).

O dióxido de carbono (CO_2) é o solvente mais utilizado em extração EFS devido à sua baixa temperatura e pressão críticas (73,74 bar e 31,1 ºC, respectivamente), o que o torna perfeito para a extração de compostos termossensíveis. O CO_2 também não é tóxico, não é inflamável e é facilmente separado do extrato. Compostos apolares são o alvo da SFE com CO_2. No entanto, quando são adicionados co-solventes, como etanol ou água por exemplo, a polaridade da mistura é modificada, e então é possível extrair também compostos polares (TEMELLI, 2009; MELO et al., 2014; COSTA et al., 2017). Um típico aparelho SFE é mostrado na Figura 4.

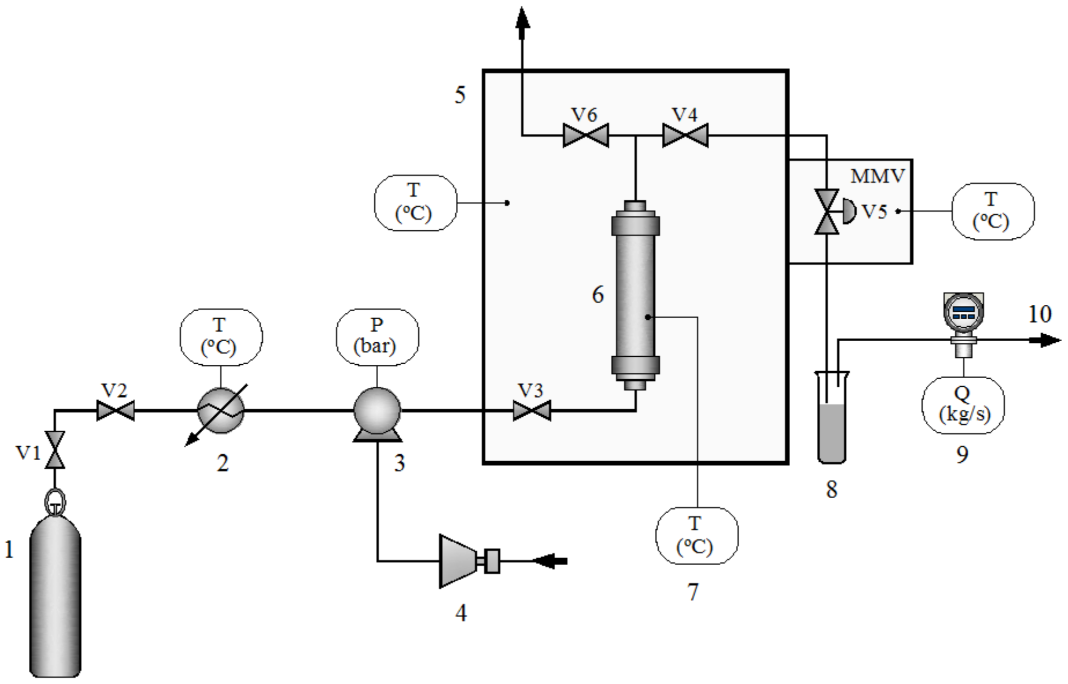


Figura 4. Aparato de extração por fluido supercrítico. 1. tanque de CO_2; 2. banho de resfriamento; 3. Bomba; 4. Compressor; 5. Forno; 6. Célula extratora; 7. Monitor; 8. Frasco coletor; 9. Medidor de vazão; 10. Saída de CO_2; V1 - V6 Válvulas de controle de fluxo (BEZERRA et al., 2018).

Quanto às aplicações do óleo e da torta, ambos têm potencial para serem aplicados na produção de diversos produtos como medicamentos, molhos, sabão, vinho, álcool, biocombustíveis, entre outros (REZAEE et al., 2014; ZHANG et al., 2018). Porém, um dos usos mais frequentes da torta de palmiste é na suplementação animal, uma vez que apresenta altos teores de fibras e proteínas (AKINYEYE et al., 2011).

Portanto, a EFS, nesse caso, é ideal para a re-extração do óleo remanescente na torta, uma vez que há a manutenção dos valores energéticos da mesma.

Neste panorama, o aproveitamento de resíduos como o palmiste na produção de biocombustíveis vem sendo relatado como uma alternativa para a utilização da biomassa proveniente da agroindústria do óleo de palma (AYETOR et al., 2015; MOTA et al., 2014; TEO et al., 2017). Dentre estes biocombustíveis, o biodiesel é uma alternativa aos combustíveis de origem fóssil, pois apresenta propriedades similares às do diesel. É uma fonte renovável de energia, e quando comparado ao diesel é biodegradável, apresenta menor toxicidade, menor teor de compostos sulfurosos e aromáticos e menor emissão de partículas como hidrocarbonetos, monóxido e dióxido de carbono (PRADO et al., 2014; FAROBIE et al., 2016).

Muitos pesquisadores estudaram a produção de biodiesel com óleo de palmiste (NGAMCHARUSSRIVICHAI et al., 2008; BENJAPORNKULAPHONG et al., 2009; VIELE et al., 2013; ALADETUYI et al., 2014; LUCARINI et al., 2017).

O biodiesel pode ser produzido por diversos métodos como a catálise (ácida, alcalina ou enzimática), esterificação, craqueamento, radiação assistida por microondas, produção assistida por ultrassom, microemulsão, transesterificação e processo supercrítico (BORA et al., 2016; BEZERRA et al., 2018; FATIMAH et al., 2018). A transesterificação ou alcoólise é a técnica mais utilizada comercialmente para a produção de biodiesel. A reação ocorre entre uma fonte de triglicerídeos e um álcool de cadeia curta, na presença ou não de um catalisador, produzindo ésteres e glicerol. A reação consiste em uma sequência de três etapas consecutivas e reversíveis como mostrado na Figura 5. Na primeira etapa ocorre a conversão dos triglicerídeos em diglicerídeos, estes em monoglicerídeos e por último, estes, em glicerol, obtendo-se um mol de éster a partir da cadeia de glicerídeo de cada etapa reacional (MUSA et al., 2016; BEZERRA et al., 2018; MANSIR et al., 2018).

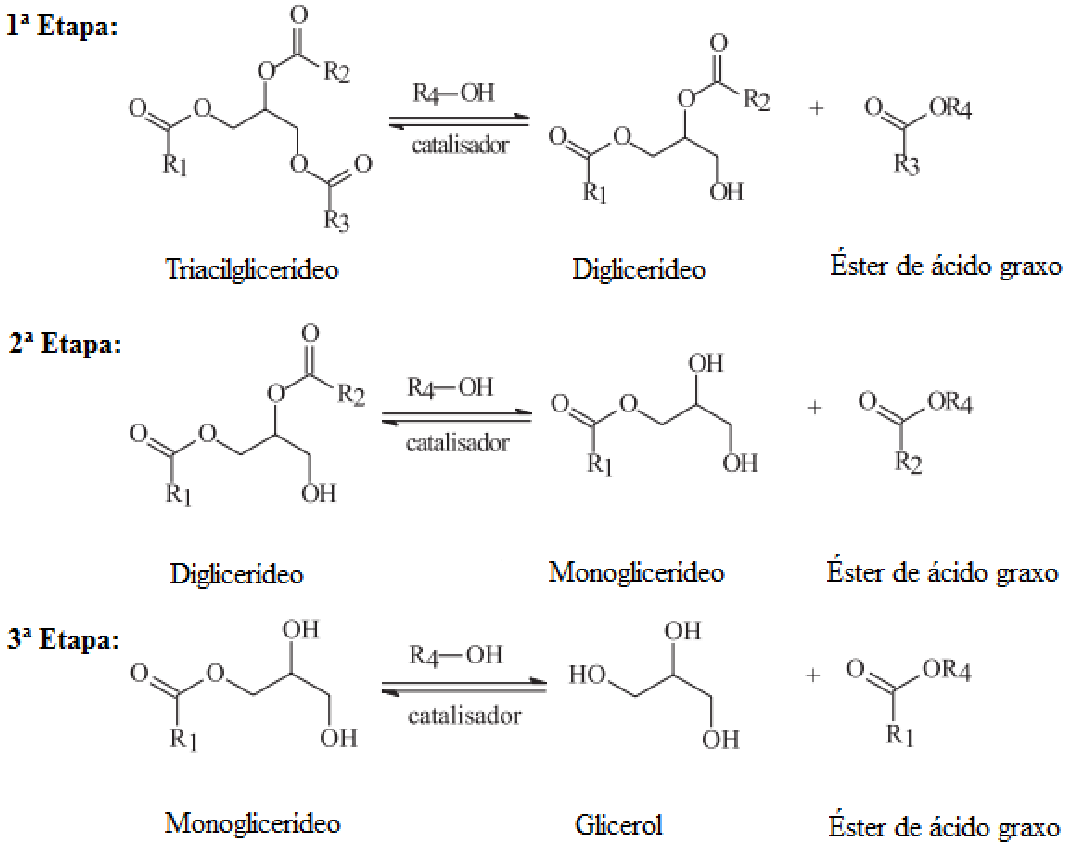


Figura 5. Etapas reacionais da transesterificação de ácidos graxos (Fonte: Adaptado de SALAM et al., 2016; MANSIR et al., 2018).

A transesterificação é dependente de fatores como o tipo de álcool e razão molar (álcool:óleo) utilizados, temperatura reacional, catalisador e quantidade utilizada, tempo reacional e características da matéria-prima. De acordo com a escolha do álcool, haverá diferença no seu consumo, nas condições da reação e de separação. Os principais álcoois utilizados são o metanol, etaaol, butanol, propanol e isopropanol. Dentre estes, o metanol é o mais empregado, pois quando comparado a outros solventes é relativamente mais barato, mais reativo e é mais facilmente separado do glicerol após a reação. Estequiometricamente, para que a alcoólise ocorra, deve haver uma razão molar de 3:1 de álcool para triglicerídeo, entretanto, a utilização de excesso de álcool no meio reacional é empregada para promover um aumento no rendimento em ésteres e para permitir a separação das fases a partir do glicerol formado (MARX, 2016; MUSA et al., 2016; MANSIR et al., 2018).

A transesterificação pode ser realizada por processos catalíticos ou não catalíticos, podendo diversos tipos de catalisadores serem utilizados na síntese. Quando há a formação de apenas uma fase com os reagentes eles são definidos como homogêneos (enzimas, ácidos e bases); e quando o catalisador está em uma fase separada à dos reagentes, estes são denominados de heterogêneos (zeólitas, óxidos e sais inorgânicos, resinas trocadoras de íons, etc.) (KUSS et al., 2015; FATIMAH et al., 2018).

Outros métodos de transesterificação, ditos não convencionais, vêm sendo aplicados recentemente. Dentre estes, pode-se destacar a transesterificação por tecnologia supercrítica. A técnica ocorre, em geral, na ausência de catalisadores, em condições rigorosas de temperatura e pressão com a utilização de equipamentos sofisticados e com alto requerimento energético. O processo mostra-se vantajoso, pois há a obtenção de um produto em um tempo de reação mais curto, sem desperdício de água, com alto grau de pureza e com maior tolerância a impurezas como água e ácidos graxos livres do que com as técnicas convencionais que utilizam catalisadores (RODRÍGUEZ-GUERRERO et al., 2013; SALAM et al., 2016).

A reação de transesterificação, quando realizada em condição ambiente, favorece a formação de duas fases e a transferência de massa controla a cinética até que haja a formação de ésteres. No estado supercrítico, o álcool forma uma única fase com o óleo, devido à redução na sua constante dielétrica, fazendo com que a velocidade da reação seja acelerada, pois não há a interferência da transferência de massa entre a interface para limitar a velocidade da reação. Devido à elevação da temperatura e pressão há também a modificação de outras propriedades do álcool como a viscosidade, peso específico e polaridade (FAROBIE et al., 2016; ROMAN-FIGUEROA et al., 2016; BEZERRA et al., 2018).

A Tabela 1 apresenta alguns trabalhos publicados nos últimos anos referentes à transesterificação pelo método supercrítico, com rendimentos em ésteres variando entre 56,2 e 99,3%, empregando-se temperatura em uma faixa de 150 a 350 °C, pressão de 68 a 200 bar e razão molar de álcool para óleo de 40:1 a 50:1.

Tabela 1**.** Trabalhos publicados nos últimos 5 anos (2013-2018) referentes a transesterificação pelo método supercrítico

Óleo	**Solvente**	**T (°C)**	**P (bar)**	**τ (min)**	**RM**	**R (%)**	**Referência**
Palmiste	Methanol	325	180	20	42:1	93.7	SAWANGKEAW et al. (2011)
Rícino	Etanol	350	145	10	40:1	56,2	RODRÍGUEZ-GUERRERO et al.

							(2013)
Colza	Etanol	350	120	20	42:1	91,9	MICIC et al. (2014)
Palma	Ethyl acetate	350	200	20	50:1	78,3	Sootchiewcharn et al. (2015)
Canola	1-propanol	350	200	30	40:1	93,8	FAROBIE et al. (2016)
Castor	Metanol	~265	68	5	50:1	96,3	TORRENTES-ESPINOZA et al. (2017)
Palma	Etanol	150	200	60	40:1	99,3	BEZERRA et al. (2018)

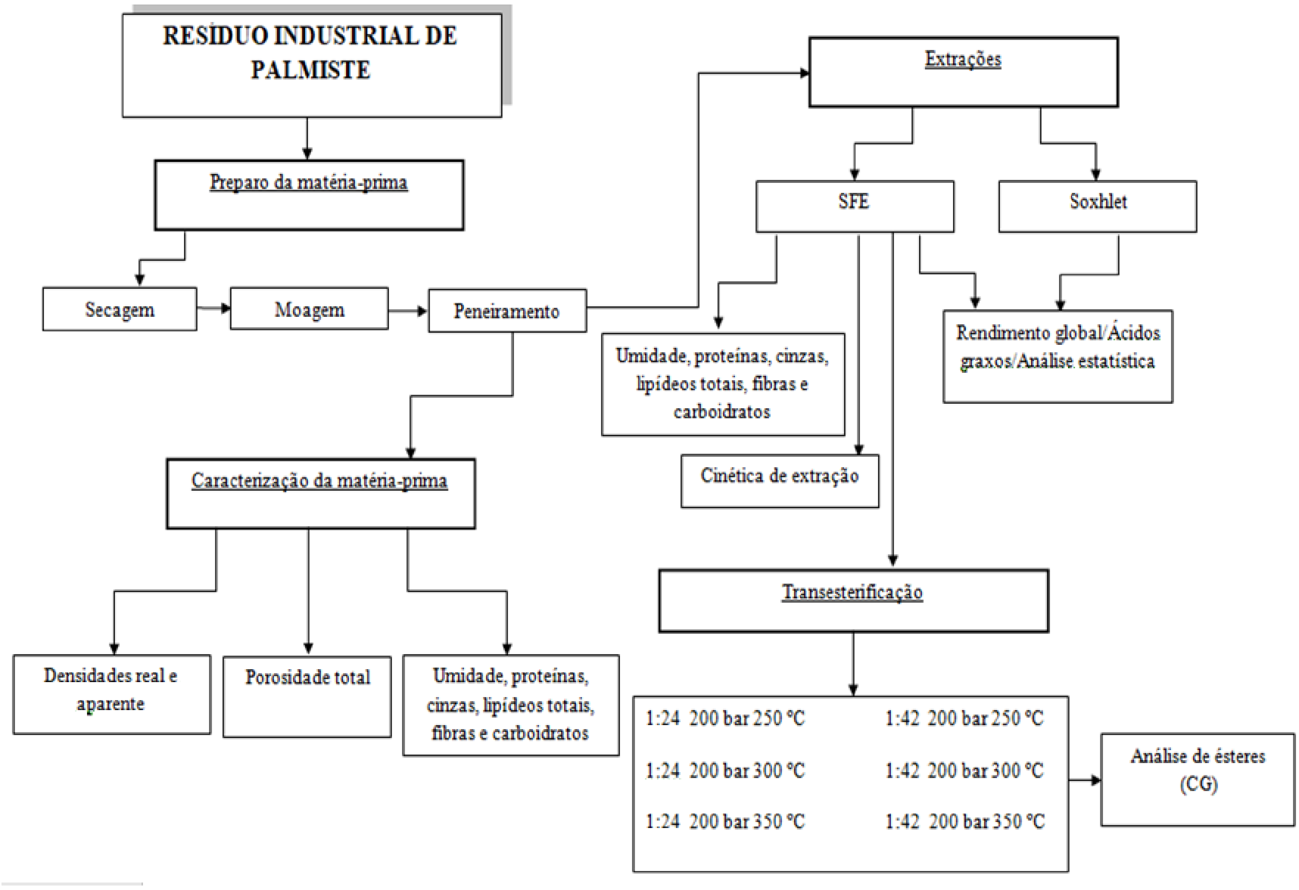
T: temperatura; P: pressão; τ: tempo; RM: razão molar (álcool:óleo); R: rendimento em ésteres; NI: não informado

Assim como no método convencional, a transesterificação supercrítica também pode ocorrer na presença de catalisadores ou cossolventes como hexano, heptano, tetrahidrofurano, tolueno, nitrogênio, dióxido de carbono e óxido de cálcio. É referido na literatura que a utilização de um cossolvente em conjunto às condições supercríticas pode reduzir o ponto crítico do álcool influenciando no aumento da miscibilidade da interface entre o álcool e o óleo no processo da transesterificação, fazendo com que se possa operar com menores temperaturas, pressões e quantidades de álcool (LIM e LEE, 2013; MUPPANENI et al., 2013).

A transesterificação pelo método supercrítico pode ser economicamente viável apesar do alto custo operacional (altos requisitos de energia e custos com equipamentos), através do melhoramento da técnica, como por exemplo, pela adição de cossolventes adequados acarretando na redução do ponto crítico da mistura, diminuindo o tempo, razão molar (álcool:óleo), pressão e temperatura reacionais (MICIC et al., 2014; MUPPANENI et al., 2013; KUSS et al., 2015).

Desta forma, o objetivo deste trabalho foi realizar o processo de transesterificação metanólica em meio supercrítico de óleo de palmiste obtido através do resíduo industrial por prensagem mecânica, sendo este extraído com dióxido de carbono supercrítico.

2. RESUMO GRÁFICO DO TRABALHO



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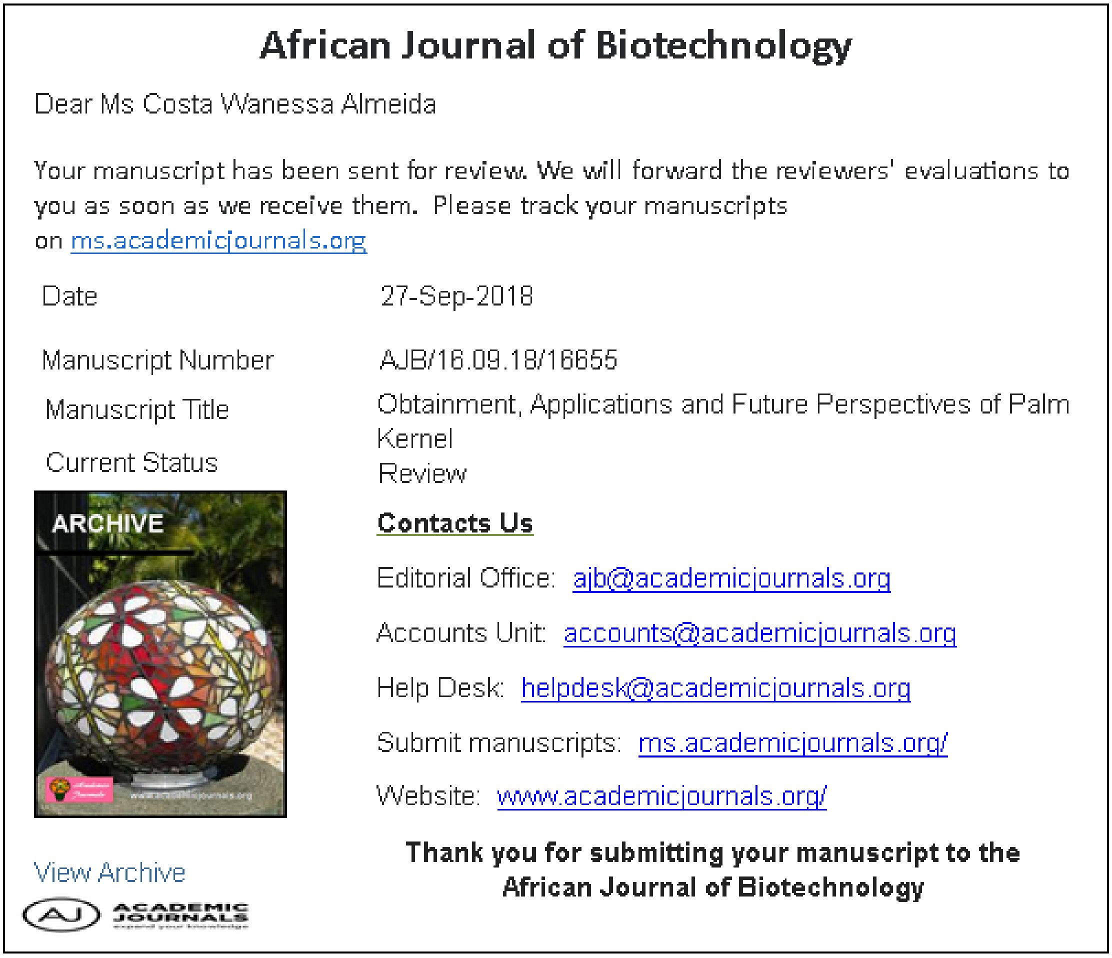
CAPÍTULO 3

ARTIGO (MINIREVIEW) INTITULADO “Obtainment, Applications and Future Perspectives of Palm Kernel”



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Obtainment, Applications and Future Perspectives of Palm Kernel

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ABSTRACT

Of African origin and with an estimated world production of 6.85 million tons, palm kernel oil contributes with about 3% of the total world production of oils and fats. With such production, the world waste generation was about 10,026 x 10^3 tons in 2017, which represents an important environment issue. The present work aimed to review the literature on the main methods of extraction, applications, and future perspectives of *Elaeis guineensis* Jacq., with emphasis on its seed: palm kernel. Regarding its main applications, biodiesel production was highlighted, since the biomass generated can be used as a substitute for fossil fuels in energy production.

Keywords: *Elaeis guineensis* Jacq., palm kernel, extraction of vegetable oils, biodiesel.

INTRODUCTION

Palm kernel is an oleaginous seed found in *Elaeis guineenses* Jacq. fruits. Historically, the demand for its grains was much higher than that for oil, due to its high consumption. Progressively, the export of grains increased considerably along with the demand for palm kernel oil, beginning their exports around 1832. The export growth rate declined a few decades after the Second World War (Atinmo and Bakre, 2003; Corley and Tinker, 2016).

The palm kernel crop has important socioeconomic representation for the countries that produce it. They are grown both by smallholders on family farms and on large-scale plantations (Kusumaningtyas and Van Gelder, 2017). Currently, palm kernel is among the world's largest oilseeds, with estimated production of 18.59 million tons in 2017 (USDA, 2018). Its main world producers are Indonesia, Malaysia, Thailand, Nigeria and Colombia, but Colombia and Thailand are the countries with the highest production growth rate (Index Mundi, 2018).

Palm kernel has higher productive potential compared to other oilseeds production costs (Zimmer, 2016), being considered as one of the crops responsible for supplying the vegetable oil world demand (Corley, 2009). It also presents production of approximately 10% of the total palm oil, being able to reach 0.4 to 0.6 MT of Palm Kernel Oil (PKO) per hectare (Sunilkumar et al., 2015), representing 3.24% of seeds oils and fats production, with a 6.5% annual growth rate (OWA, 2016; FAO, 2015, 2017).

The palm kernel oil can be extracted by several methods, such as: mechanical extraction, solvent extraction, microemulsion, and extraction with supercritical fluids (Norhaizan et al., 2013). This oil production presents social and environmental benefits, such as the generation in employment and income, and consequently improvement in the producer’s life quality, and trade development (Sargeant, 2001; Basiron, 2007). Regarding progress on culture and also new areas of palm kernel applications, several alternatives have been studied, from improvements in crop and new methods to obtain the oil, to the development of new products such as biofuels, cosmetics, and food products (Da Silva and Batalha, 2013; Cros et al., 2015; Bashir et al., 2015; Da Silva and Engelmann, 2017).

With such expressive production, this crop generates challenges to balance the increase of yields with the deforestation reduction. Also, reduction of industrial residues from oil extraction processes are highly required, since 10,026 x 10^3 tons of Palm

Kernel Cake (PKC) were generated in 2017 (Norhaizan et al., 2013; Fitzherbert et al., 2008; Koh and Wilcove, 2008; Index Mundi, 2018).

Thus, the objective of this study was to present the main aspects of palm kernel oil obtainment, as well as the current scenario of applications, the management of extraction residues, and their technological advances.

OBTAINING METHODS OF PALM KERNEL OIL

Currently, there are several methods that have been used in the process of obtaining greases, such as solvent extraction, mechanical pressing, supercritical fluids, ultrasound, and others (Borges et al., 2016). In this research, the focus will be on the most used method for extracting palm kernel oil: mechanical pressing. Extraction by supercritical fluids will be approached as an alternative to recover the remaining oil of palm kernel cake.

Mechanical pressing extraction

Pressing may be defined as a compression step in which a liquid is exuded from a porous matrix. In the industry, oilseed extraction is performed with continuous screw presses. This step does not require heat input or organic solvents, thus being the least expensive part of the process (Subroto et al., 2015).

This type of oil extraction requires seed pre-treatment, which may include size reduction, cracking, drying, sieving, etc. This is necessary to efficiently extract the oil from the kernels. At first, they must be cleaned of materials that may contaminate the products and cause damage to the equipment. In order to remove metal residues, stones, sand, and other undesirable materials, magnetic separators and vibrating screens are commonly installed (Savoire et al., 2013; Rombaut et al., 2015; Firdaus et al., 2017). During expression, the raw palm kernel oil is separated for clarification and the residue is cooled and stored in a warehouse. See Figure 1.

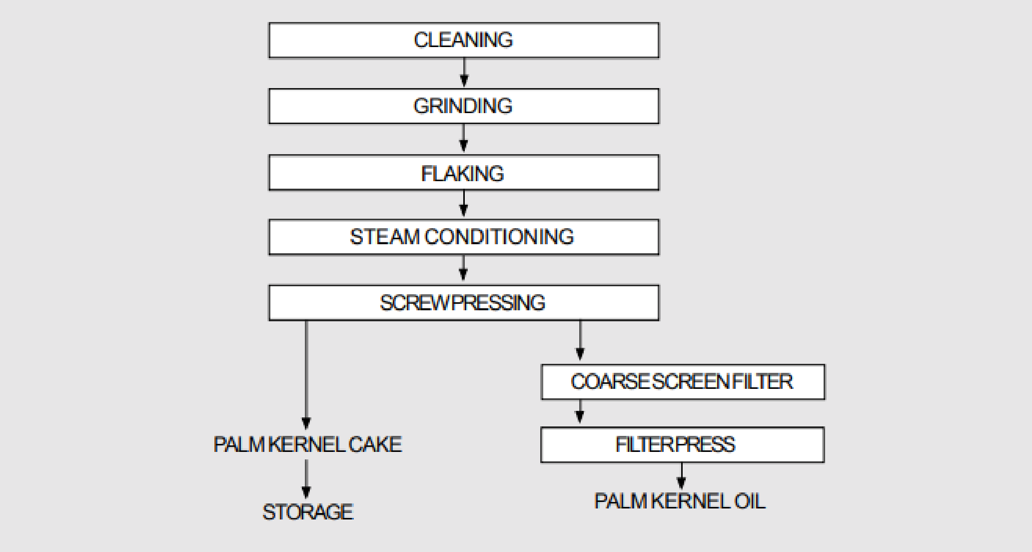

Figure 1: Mechanical extraction simplified flow chart of palm kernel oil (Sue, 2004)

Malaysia produced 2.4 million tons of Palm Kernel Cake (PKC) out of 4.7 million tons of palm kernel, in world at 2012 (Ibrahim, 2013). As the organic solvent extraction cost is high, and the solvent recovery is difficult, the mechanical process is the most currently used. The content of PKC includes high contents of fiber, manganese, iron, and zinc (Akinyeye, 2011). The chemical and mineral compositions of PKC are shown in Table 1.

Table 1: PKC mineral content and chemical composition from mechanical pressing (%). Adapted from Alimon (2004).

Calcium (%)	0.21 – 0.34
Phosphorus (%)	0.48 – 0.71
Magnesium (%)	0.16 – 0.33
Potassium (%)	0.76 – 0.93
Sulphur (%)	0.19 – 0.23
Copper (ppm)	20.5 – 28.9
Zinc (ppm)	40.5 – 50.0
Iron (ppm)	835 – 6130
Manganese (ppm)	132 – 340
Molybdenum (ppm)	0.70 – 0.79
Selenium (ppm)	0.23 – 0.30

Dry matter	88 – 94.5
Crude protein	14.5 – 19.6
Crude fibre	13.0 – 20.0
Esther extract	5.0 – 8.0
Ash	3.0 – 12.0
Nitrogen-free extract	46.7 – 58.8
Neutral detergent fibre	66.8 – 78.9
Metabolisable energy ($MJ.kg^{-1}$)	
Ruminants	10.5 – 11.5
Poultry	6.5 – 7.5
Swine	10.0 – 10.5

With such composition, many studies have been carried out regarding the inclusion of PKC in animal feed (Rhule, 1996; Zahari and Alimon, 2004; Orunmuyi et al., 2005; Adesehinwa, 2007). According to Alimon (2004), PKC is one of the most flexible feed ingredients, since it can be used in all types of animal rations, consequently reducing conventional feedstuffs importation. However, quantities of anti-nutritional factors present may limit their feed value and usage. In this case, enzymes can be added in animal diets in order to supplement the enzymes already present in the digestive system (Zamani et al., 2017). Besides the use in animal feed, fibers and shells can still be used as feed in steam boilers, being useful as raw material in the coal industry (Zhang et al., 2018). On the other hand, refined oil has applications in products of the most varied sectors such as in the food, cosmetic, pharmaceutical, oleochemical, and chemical industries, among others (Rezaeeet al., 2014; Septevani et al., 2015).

Embrandiri et al., (2012), Ibrahim (2013) and Subramaniam et al. (2013) specifically use the screw press technique to extract palm kernel oil. Ikechukwu et al. (2012) designed an expeller pilot plant to extract 200 Kg of oil/day. The plant was tested with an initial input of 59.52 Kg of palm kernel per hour, for 10 h. As a result, 200.05 Kg of high-quality palm kernel oil was obtained.

Regarding the crude palm kernel oil fatty acid composition, it presents about 82.6% of saturated fatty acids, with the lauric acid as the major component, followed by myristic and oleic acids (See Table 2). Because of its saturation content, this oil is very resistant to oxidation (Ibrahim, 2013).

Table 2: PKO fatty acid composition obtained from the pressing technique. Adapted from Ibrahim (2013)

Fatty Acid	Range (%)
Caproic acid (C_6:0)	0.2 – 0.4
Caprylic acid (C_8:0)	3.2 – 4.7
Capric acid (C_{10}:0)	2.9 – 3.5
Lauric acid (C_{12}:0)	45.4 – 49.8
Myristic acid (C_{14}:0)	15.4 – 17.2
Palmitic acid (C_{16}:0)	7.9 – 9.3
Stearic acid (C_{18}:0)	1.9 – 2.3
Oleic acid (C_{18}:1)	13.7 – 17.0
Linoleic acid (C_{18}:2)	2.1 – 2.9
Total saturated	82.6

Supercritical Fluids Extraction (SFE)

Some researchers have reported that, the supercritical fluid extraction of palm kernel oil from palm kernel, obtaining yields up to 49.9% (Norulaini et al., 2004; Zaidul et al., 2007). In the work of Hossain et al. (2016), the optimum conditions of palm kernel oil extraction were pressure of 44.6 MPa, temperature of 60 ºC and extraction time of 50 min, whose yield was approximately 49.2%. A typical SFE apparatus is shown in Figure 2.

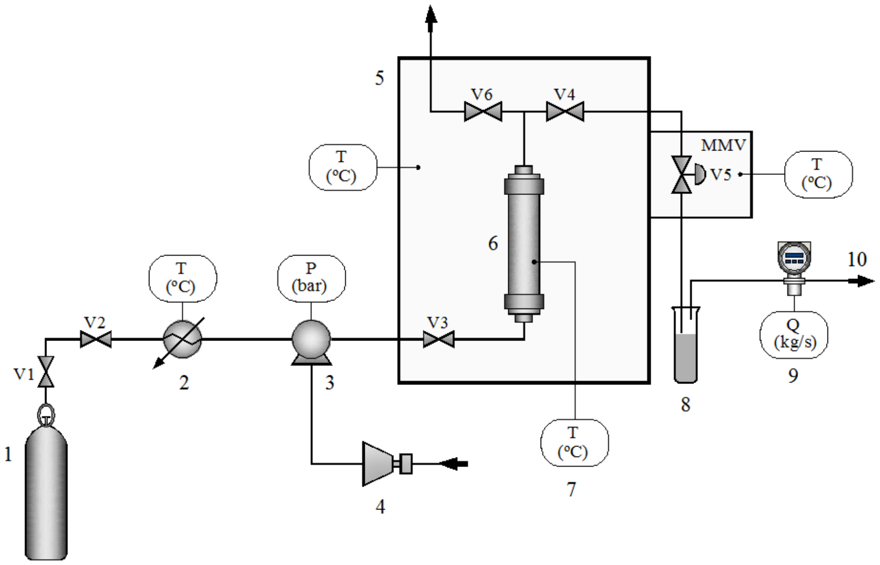

Figure 2. SFE apparatus. 1. CO_2 tank; 2. Cooling bath; 3. Pump; 4. Compressor; 5. Oven; 6. Extractor vessel; 7. Monitor; 8. Vial; 9. Flowmeter; 10. CO_2 Outlet; V1 – V6

Flow control valves (Bezerra et al., 2018).

Zaidul et al. (2006) applied supercritical CO_2 to fractionate palm kernel oil and concentrate C16–C18: 2 fatty acid constituents. Pressures ranging from 34.5 to 48.3 MPa at 80 ºC were the best operating conditions to optimize the yield up to 99.6%. Ab Rahman et al. (2012) reported the re-extraction of the screw press residues using supercritical carbon dioxide. In their research, different particle sizes were tested for the highest oil yield, obtaining yields up to 9.26%, at 70 ºC and 41.36 MPa, sample size of 150 μm, carbon dioxide flow rate of 2.0 mL/min, during 60 minutes. The increase in pressure and temperature, and the reduction in particle size favored the maximum extraction yield, as can be seen in Figure 3.

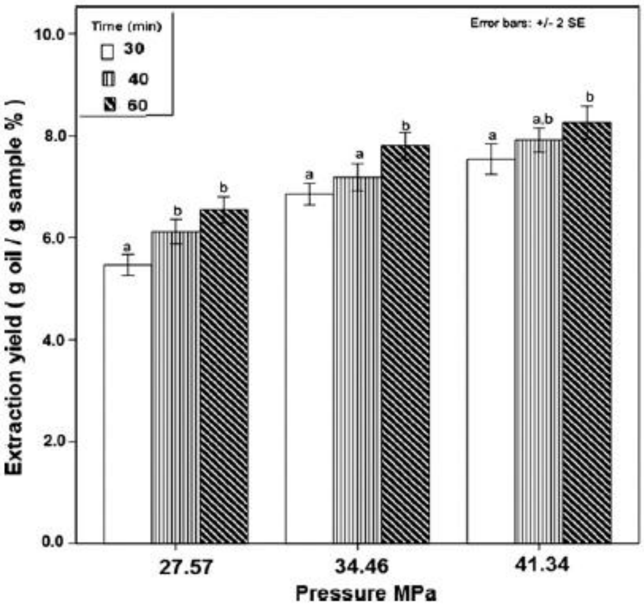

Figure 3: Effect of pressure on extraction yield at 70ºC operating temperature, 1.5 mL/min flow rate, and ≤ 150 μm particle size (Ab Rahman et al., 2012).

Krishnaiah et al. (2012) also obtained PKO from PKC, using supercritical carbon dioxide and ethanol as co-solvent. The fatty acid profile and the content of vitamin E and sterols were evaluated. The operating conditions were 19.8 MPa pressure, and 51 ºC temperature. Amounts of 45, 50, and 100 mL of ethanol were used in the expression runs. They found out that the highest quantity of ethanol provided the highest extraction yield. Also, lauric, myristic, and oleic acids, as well as, two types of vitamin E (alpha-tocopherol and alpha-tocotrienol) were present in the oil samples. Table 3 shows the extraction yield of each run and Table 4 shows the quantitative analysis of fatty acids, vitamin E, and sterols.

Table 3: Amount of oil extracted in each run (Krishnaiah et al., 2012)

Sample	Pure CO_2	45 mL ethanol	50 mL ethanol	100 mL
Weight before (g)	62.736	62.758	61.770	61.662
Weight after (g)	62.998	63.350	63.601	65.330
Weight of oil content (g)	0.262	0.592	1.831	3.668

Table 4: Quantitative analysis of fatty acids, vitamin E, and sterols. Adapted from Krishnaiah et al. (2012)

	Fatty acid (%)			Vitamin E (ppm)		
Sample	Lauric	Myristic	Oleic	α-tocopherol	α-tocotrienol	Sterol
Pure CO_2	59.3	21.1	19.5	230.0	300.0	650.0
45 mL ethanol	59.4	21.1	19.5	229.2	302.0	660.4
50 mL ethanol	59.5	21.2	19.3	228.0	300.6	677.2
100 mL ethanol	59.5	21.0	19.5	233.3	309.7	678.0

Ab Rahman et al. (2011) evaluated the application of supercritical fluid extraction as a method that maintains the PKC nutritional components. They compared the nutritional composition of palm kernel fibre derived from three PKC samples: supercritical PKC with test (SC-PKt), supercritical PKC without test (SC-PK), and PKC from palm oil mill. Carbon dioxide was used as solvent at 80 °C temperature and 41.36 MPa pressure. Total dietary fibre, crude fibre, crude protein, ash, and moisture were determined and compared with PKC from palm oil mill. The results are shown in Table 5.

Table 5: PKC composition with testa, without testa, and from palm mill. Adapted from Ab Rahman et al. (2011)

Samples	Palm kernel with test	Palm kernel without test		Palm kernel cake	
	Before SFE PKt	After SFE SC-PKt	Before SFE SC-PK	After SFE SC-PK	Without SFE
Composition					
Totally dietary fibre (%)	61.58	63.03	57.78	58.96	60.71

Crude fibre (%)	8.99	8.49	7.29	7.23	15.17
Moisture (%)	10.51	3.26	11.86	3.44	6.84
Crude protein (%)	15.61	14.40	15.01	14.06	13.56
Ash (%)	8.58	4.34	3.96	3.55	13.92

They concluded that supercritical fluid extraction is a great technique to improve the fiber production and oil separation, without affecting its nutrient composition. SC-PKt proved to be superior compared to SC-PK and PKC from palm oil mill. SC-PKt became higher in dietary fiber and protein, while moisture and ash contents reduced significantly. They highlighted the fact that such cake might be used for human consumption in the future.

USE OF PALM KERNEL FOR BIOFUEL PRODUCTION

The use of residues, such as palm kernel in biofuels production has been reported as an alternative for the use of biomass from palm agro-industry (Ayetor et al., 2015; Sukiran et al., 2017). Among these biofuels, biodiesel is an alternative to fossil fuels, because it has similar properties to those of diesel, it is a renewable source of energy, and when compared to diesel it is biodegradable, it presents lower toxicity, lower content of sulfurous, lower aromatic compounds, and lower emissions of particulates such as hydrocarbons, monoxide, and carbon dioxide (Prado et al., 2014; Farobie et al., 2016).

Conventional production of biodiesel

Many researchers have studied the biodiesel production with palm kernel oil (Ngamcharussrivichai et al., 2008; Benjapornkulaphong et al., 2009; Viele et al., 2013; Aladetuyi et al., 2014; Lucarini et al., 2017). Alamu et al. (2007) performed the PKO transesterification process with ethanol, using KOH as the alkali-catalyst. 100 g of PKO, different amounts of KOH, and 20 g of ethanol were used. Reaction time was equal to 100 minutes.

This type of production requires the following steps: a) transeterification process; b) settling, in which the reaction mixture stands in order to facilitate phase separation (biodiesel and glycerol) by gravity; and c) washing, in which water is added at 1:3 ratio (biodiesel:water) in order to remove glycerol, soap, and fatty acids residues.

In their work, the PKO biodiesel highest yield was of 95.8% with 1.0% KOH concentration and 20.0% ethanol, at 60 ºC for 120 minutes. Unreacted alcohol, residual catalyst and emulsion removed during the washing stage count as process losses. Figure 4 shows the PKO biodiesel variation (%) with KOH concentration (%).

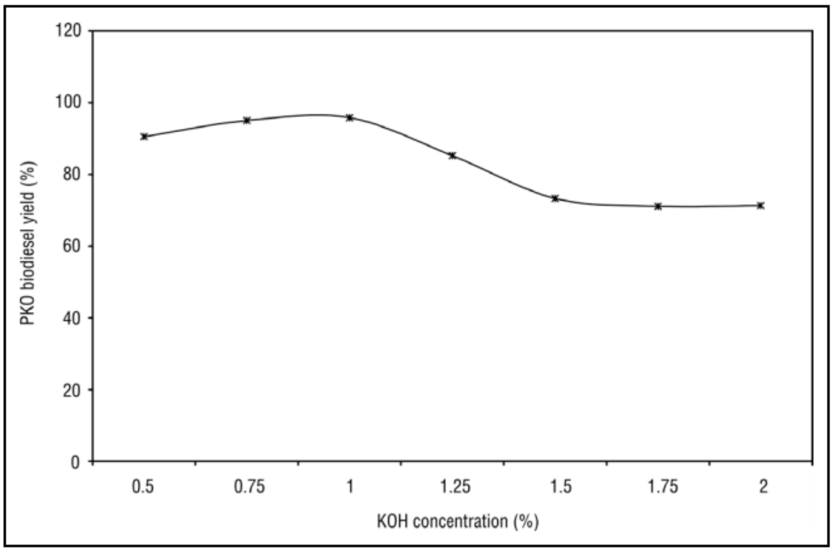

Figure 4: Variation of KOH concentration (%) with PKO biodiesel yield (%) through traditional experimentation technique (Alamu et al., 2007)

Jitputti et al. (2006) used ZrO_2, ZnO, $SO4^{2-}/SnO_2$, $SO4^{2-}/ZrO_2$, KNO_3/KL zeolite, and KNO_3/ZrO_2 as heterogeneous catalysts for PKO biodiesel production. The transesterification process was carried out using 1:6 (oil: methanol) molar ratio, with a certain amount of catalyst. The temperature was equal to 200 ºC and the mixture stirred at 350 rpm. Then, the catalyst was separated from the product by filtration. Phase separation isolated the methyl esters from glycerol, which was removed and the remaining phase (biodiesel) was washed with distilled water, and dried by adding sodium sulfate. Table 6 shows the PKO biodiesel yield according to the catalyst used.

Table 6: Crude palm kernel oil transesterification by solid catalysts. Adapted from Jitputti et al. (2006)

Run	Catalyst	Methyl ester content (wt.%)	Methyl ester yield (wt.%)
1	-	32.3	30.4

2	ZrO_2	69.0	64.5
3	ZnO	98.9	86.1
4	SO_4^{2-}/SnO_2	95.4	90.3
5	SO_4^{2-}/ZrO_2	95.8	90.3
6	KNO_3/KL zeolite	77.8	71.4
7	KNO_3/ZrO_2	78.3	74.4

They concluded that the catalysts SO_4^{2-}/ZrO_2 and SO_4^{2-}/SnO_2 can yield up to 90.3% of PKO methyl esters. Also, one-hour reaction time is enough for the amount of methyl esters to reach its highest yield.

Alamu et al. (2008) also produced PKO biodiesel through the conventional method, obtaining yield of 95.8%. They used 100 g of PKO, 20.0 g of ethanol, and 1.0% of NaOH, at 60 °C for 90 minutes.

Biodiesel production by supercritical method

Other non-conventional transesterification methods have been recently applied. Among these, it is possible to emphasize the supercritical transesterification technology. The technique generally occurs in the absence of catalysts, under stringent conditions of temperature and pressure with the use of sophisticated equipment and with high energy requirements. The process is advantageous, since a product is obtained at a shorter reaction time, no waste of water, high purity, and with greater tolerance to impurities such as water and free fatty acids than with conventional techniques using catalysts (Rodríguez-Guerrero and Rosa, 2013; Salam et al., 2016). See Figure 5.

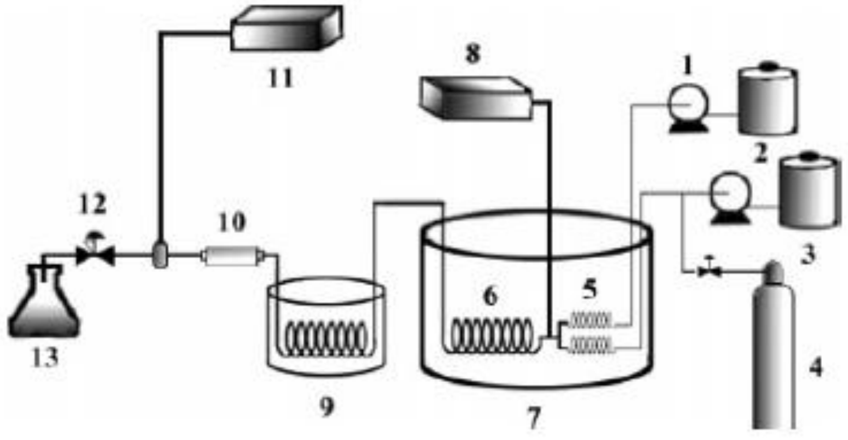

Figure 5: Schematic diagram of the continuous transesterification reactor system. 1. High-pressure pumps, 2. methanol reservoir, 3. vegetable oil reservoir, 4. nitrogen cylinder, 5. preheaters, 6. reactor, 7. salt bath, 8. temperature monitoring system, 9. cooling bath, 10. inline filter, 11. pressure monitoring system, 12. back pressure regulator, and 13. sample collector (Bunyakiat et al., 2006).

The transesterification reaction, when performed under ambient conditions, favors the formation of two phases and the mass transfer controls the kinetics until there is esters formation. In the supercritical state, the alcohol forms a single phase with the oil, due to the dielectric constant reduction, causing the acceleration on the reaction speed, since there is no interference of the mass transfer between the interface to limit the reaction speed. Due to the elevation of temperature and pressure there is also the modification of other properties of alcohol such as viscosity, specific gravity, and polarity (Farobie et al., 2016; Román-Figueroa et al., 2016; Bezerra et al., 2018).

Especially using the supercritical method for PKO transesterification, Bunyakiat et al. (2006) achieved, in only 400 s, a methyl ester conversion of 96% at 1:42 (oil: methanol) molar ratio, 350 ºC and 19 MPa. They found out that by increasing the temperature from 270 to 300 ºC and 350 °C, methyl ester conversions also increased. Regarding the molar ratio, when the methanol content increased, methyl ester conversion increased as well. This is favorable inasmuch as excess alcohol is desirable and also because it contributes to reduce the mixture critical temperature. Figure 6 and 7 show the effect of temperature and methanol: oil molar ratio, respectively, on the methyl esters yield.

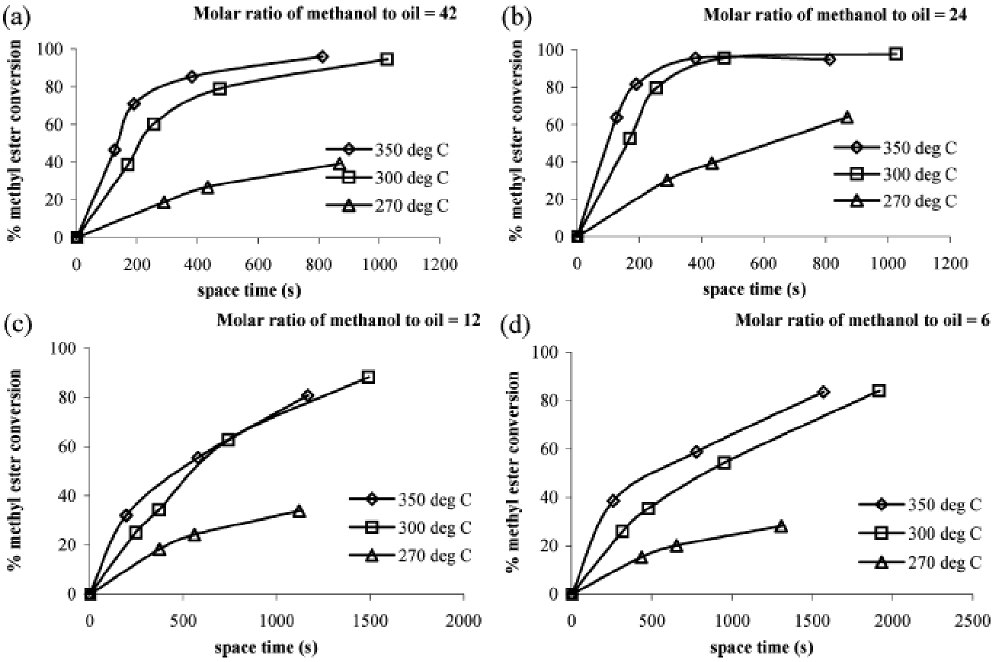

Figure 6: Effect of temperature on the % methyl ester conversion at various molar ratios of methanol-to-palm kernel oil, P = 19 MPa. (a) 42, (b) 24, (c) 12, (d) 6 (Bunyakiat et al., 2006)

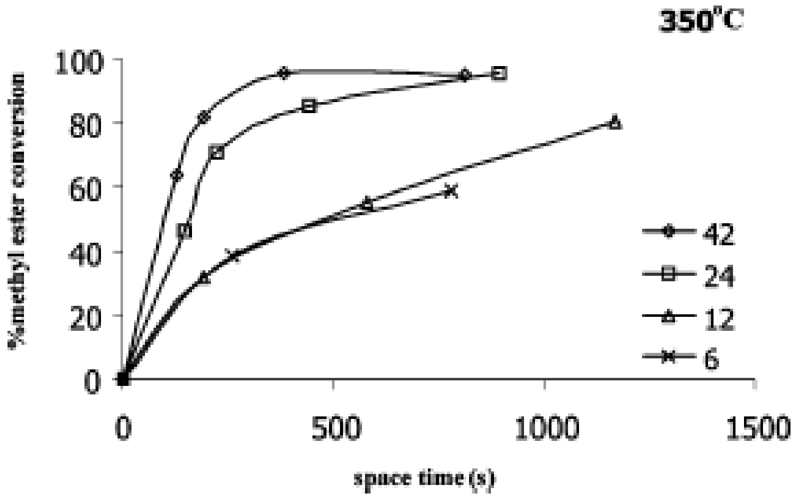

Figure 7: Effect of molar ratio of methanol-to-palm kernel oil on the % methyl ester conversion at 350 °C, 19.0 MPa (Bunyakiat et al., 2006)

In the same way, Sawangkeaw et al. (2011) obtained 93.7% of alkyl esters conversion, with molar ratio, of 1:42, 325 ºC and 18.0 MPa. Performing a process optimization, they found out that to reach a methyl esters content of over 96.5%, the minimal molar ratio is 1:40.

The supercritical method transesterification can be economically feasible despite the high operational cost (high energy requirements and equipment costs), through the technique improvement, for example with the addition of suitable cosolvents causing reduction of the mixture critical point, decreasing time, alcohol-to-oil molar ratio, reaction pressure, and temperature (Muppaneni et al., 2013; Micic et al., 2014; Kuss et al., 2015).

FINAL CONSIDERATIONS

The abundant and inexpensive availability of PKC that comes from the mechanical pressing process has attracted attention due to its potentiality to become an energy source and an effective ingredient in the feed formulation for animals, since it is rich in fibers, protein, and energy contents. However, in order to overcome some anti-nutritional factors present enzymes addition has presented promising results.

The palm kernel oil extraction main product, due to its characteristics and physic-chemical properties, is an excellent raw material for specific applications, such as cosmetics production, substitutes for cocoa butter, production of various foods, and biofuels, such as biodiesel.

The supercritical extraction has proved to be an excellent method to recover the PKC remaining oil, since high oil yields can still be obtained. Regarding biofuels production, the supercritical transesterification was presented as an alternative to the conventional method. Studies showed that increasing temperature and molar ratio of methanol to oil also increase the yield of esters formed. Although supercritical technique provides short-time reactions and eliminates the need for catalysts, this method presents some drawbacks due to the high energy consumption, since conditions of high temperature and pressure are required.

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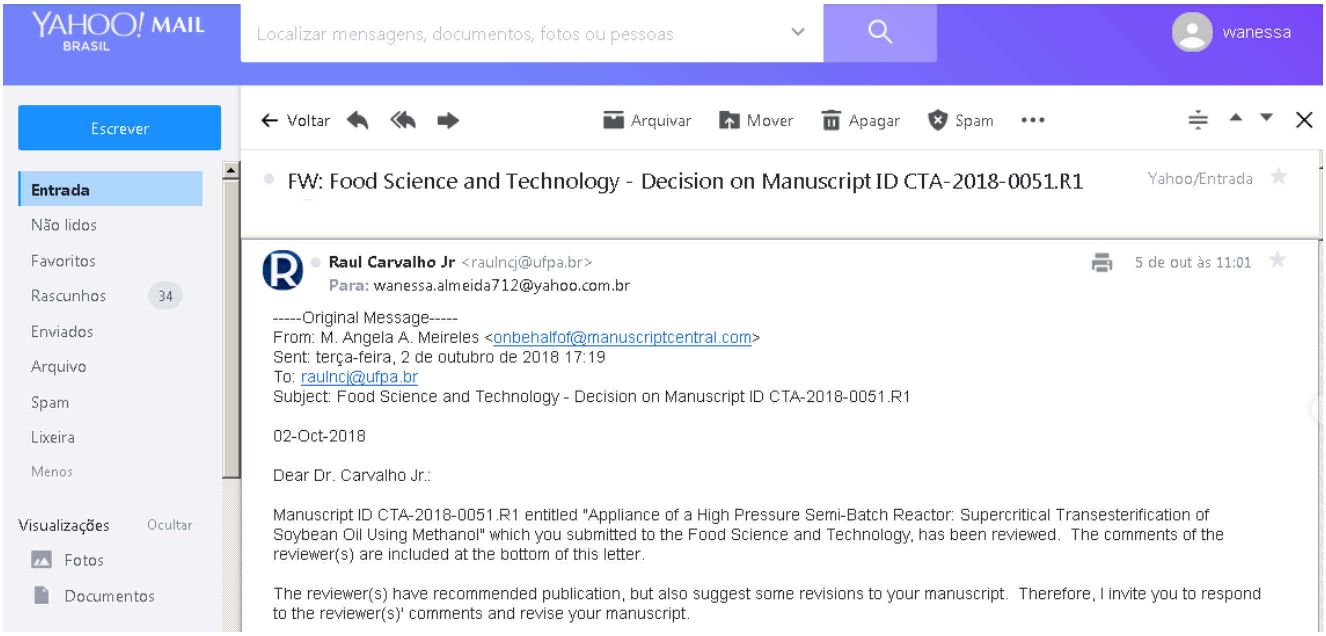
CAPÍTULO 4

VALIDAÇÃO DO REATOR SEMI-BATELADA USADO NOS EXPERIMENTOS: ARTIGO INTITULADO “Appliance of a High Pressure Semi-Batch Reactor: Supercritical Transesterification of Soybean Oil Using Methanol”



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Raul Carvalho Jr <raulncj@ufpa.br>
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Dear Dr. Carvalho Jr.:

Manuscript ID CTA-2018-0051.R1 entitled "Appliance of a High Pressure Semi-Batch Reactor: Supercritical Transesterification of Soybean Oil Using Methanol" which you submitted to the Food Science and Technology, has been reviewed. The comments of the reviewer(s) are included at the bottom of this letter.

The reviewer(s) have recommended publication, but also suggest some revisions to your manuscript. Therefore, I invite you to respond to the reviewer(s)' comments and revise your manuscript.

Appliance of a High Pressure Semi-Batch Reactor: Supercritical Transesterification of Soybean Oil Using Methanol

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Abstract

This work presents the results of a supercritical transesterification process of soybean oil using methanol, performed in a laboratory high pressure semi-batch reactor. A full description of the equipment and a standard operating procedure are also provided. Since fossil fuels are not renewable, biofuels such biodiesel, have gained attention over the past decades. Biodiesel is the result of the transesterification of triacylglycerols in vegetable oils or animal fats and it works as an alternative fuel for compression-ignition engines. Methanol was chosen to perform the reaction, at molar ratios of 1:24 (oil: alcohol) and 0.1 (CO_2:methanol), temperature of 280 ºC and pressure of 130 bar. In order to decrease the reaction time, CO_2 in the supercritical state was used as cossolvent. The yield of biodiesel produced was equal to 95.19% in only ten minutes of reaction. A high yield of methyl esters (84.41%) was detected by gas chromatography-mass spectrometry. In general, 10 compounds were identified. The component in higher concentration was linoleate, followed by methyl hexadecanoate, oleic acid methyl ester and methyl stearate. The ester conversion rate means that the process with supercritical methanol can be successfully applied to produce biodiesel.

Keywords: Autoclave, Transesterification, High-Pressure Reaction, Supercritical Conditions.

Practical Application: The development of new techniques is of great importance for the future generations, since the more the world population grows, the more energy is required to maintain life quality. This includes the production of biofuels, considering that fossil fuels are not renewable. Thus, to produce biodiesel, the supercritical transesterification corresponds to an alternative to the standard transesterification method since it does not require the use of conventional catalysts, generates less undesirable products, with a high rate of alkyl esters, in a short-time reaction.

1. Introduction

Nowadays, the need for renewable energy sources increases everyday due to the greater demand for petroleum products, which are not renewable and tends to be more expensive in the future. Another aspect of these products is that they produce a lot of harmful composites, such as carbon monoxide, nitrogen and sulfur oxides. Therefore, attention has been focused on developing renewable, biodegradable or alternative fuels, such as biodiesel to replace petroleum based fuels (Fukuda et al., 2001; Gopinath et al., 2009; Javidialesaadi & Raeissi, 2013).

Biodiesel is the result of the transesterification of triacylglycerols in vegetable oils or animal fats. It works as an alternative fuel for compression-ignition engines. Since the transesterification reaction needs a short-chain alcohol, methanol and ethanol are the most used (Bunyakiat et al., 2006; Ali et al., 2013).

At first, the transesterification is a reversible reaction (Figure 1). However, the glycerol formed is immiscible in biodiesel, greatly reducing the extent of the reverse reaction. The miscibility of glycerol in the biodiesel is a factor favoring the yield of reaction; however, the possibility of forming stable emulsions, in certain cases, may require a long period of rest for phase separation of biodiesel and glycerol (Atadashi et al., 2011; Lourenço et al., 2009).

In biodiesel production with base catalysts, besides the transesterification reactions, saponification of alkyl esters or of triacylglycerols themselves may also occur. Saponification is the formation of soap, i.e., salts of fatty acids, which can also occur due to a high content of free fatty acids in oils or fats. The soap formation involves three problems: it consumes the catalyst used in the reaction; it causes an increase in viscosity or formation of gels that interferes in the reaction. Also, the presence of soap in the reaction mixture stabilizes the biodiesel/glycerol emulsion. A technical problem is also related to the use of biodiesel with high soap content: engine damage due to fouling and corrosion (VanGerpen, 2009; Ma & Hanna, 1999; Meher et al., 2006).

The biodiesel production may involve the use of catalysts: acids but mostly bases (hydroxide or sodium alkoxide or potassium). It has the advantage of being carried out at room temperature and still be faster than the transesterification catalyzed by acids, which needs to be performed at elevated temperatures (170 ºC) (Rinaldi et al., 2007; Vicente et al., 2004).

Many types of vegetable oils can be used to produce biodiesel. Sunflower, corn, olive, palm and soybean oils are good examples of raw materials that are widely used in this process. Since Brazil is a great producer of soybean, its oil is one of the most used as cooking oil, in the food industry and in the transesterification technique (Geris et al., 2007). In addition, its composition of fatty acids is well known, consisting mostly of linoleic, oleic and linolenic acids (KAWAZOE, 2014).

Several authors, such as Bernardes et al. 2007, Antunes et al. (2008) and Li et al. (2012) have worked with transesterification of soybean oil, and obtained high conversion of fatty acid esters. In these works, methanol and/or ethanol as the reaction alcohol, as well as different kinds of catalysts were used, such as potassium hidroxyde, zinc oxide, aluminium oxide and even enzymes. Dealing exactly with transesterification of soybean oil with supercritical alcohol and carbon dioxide, the papers of Bertoldi et al. (2009) and Cheng et al. (2010) can be highlighted.

In addition to the conventional method of producing biodiesel, another technique has been investigated over the past few years: the supercritical transesterification process. This method has been studied by many authors such as Dermibas (2005); Varma et al., (2010), Sawangkeaw et al. (2011), Anikeev & Yakovleva (2013), Tsai et al. (2013) and Ngamprasertsith et al. (2014). According to Marulanda (2012), this process has the advantage of promoting fast transesterification reactions of triacylglycerols and immediate esterification of free fatty acids without the excessive formation of glycerol and no need of a conventional catalyst. It also forms a homogeneous phase of the alcohol and triacylglycerols mixture.

The use of supercritical CO_2 can affect the kinetic behavior of the transesterification reaction. This may occur due to the increase of alcohol solubility in the oil phase (Galia et al., 2011). It is reported that the methylation of fixed oils using supercritical fluids may be a viable alternative for the production of biodiesel from different plant matrices (Chen et al., 2010; Soh & Zimmerman, 2011).

The type of reactor used in transesesterification processes is also a very important factor to consider. Authors such as Spallina et al. (2017) and Pret et al. (2015) worked with the design, modeling and validation of reactors. Mjalli et al. (2009) dealt with the developing and validation of a transesterification reactor. According to Kern & Shastri (2015), this process can be carried out in a continuous or batch reactor, but the batch process is often preferred because of its flexibility and accommodation of various types of raw materials, composition, and quantity, thus making possible to satisfy specific product requirements. Lim & Lee (2011) and Goreishi & Moein (2013) also used batch reactors to transesterificate vegetable oils using methanol in supercritical conditions, obtaining high yields of fatty acid methyl esters.

In this context, the objective of this work was to evaluate the process of supercritical transesterification of soybean oil with methanol in the presence of carbon dioxide, and provide comparisons to the conventional technique.

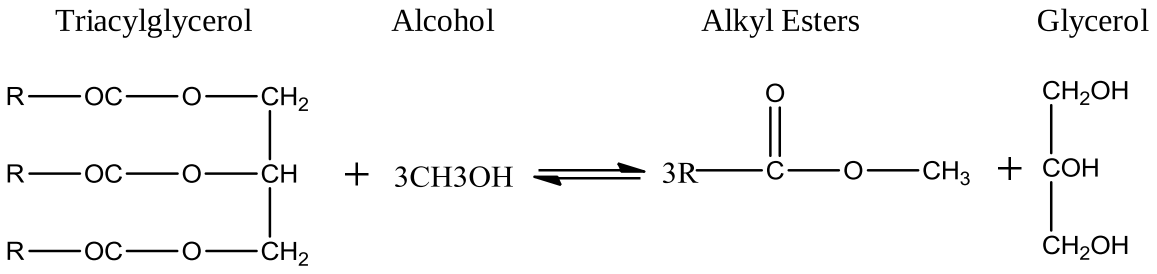

Figure 1. Overall scheme of a generic triacylglycerol transesterification with methanol

2. Materials and Methods

2.1 Equipment Description

The supercritical transesterification reaction of soybean oil with methanol and CO_2 was performed in a stainless-steel autoclave (model 2777 1000, Top Industrie, France) with internal volume of 0.095 L (0.128 x 0.152 m). To the autoclave were attached a heating collar (model 2777 1021, Top Industrie, France), a magnetic stirrer (model 616 0100, Top Industrie, FR), a cooling bath (model Q214U2, Quimis, Brazil), a thermocouple TKA 15 x 20 HMP, Erciat, France), a safety head (model 728 0350, Top Industrie, France), a rupture disk (model 728 0400, Sitec, Switzerland), a pressure transducer (model PA-Keller, Switzerland), a CO2 supply system, a sample collection system with approximately 8 mL, and a control panel (model TS1070, Monitouch Technoshot, The Netherlands). More details are in the appendix at the end of the references section.

2.2 Materials

For the transesterification process, commercial refined soybean oil (LISA, Brazil), obtained in a supermarket in Belem/Para/Brazil was used as the vegetable oil. The alcohol used was Methanol (99.9% purity, TEDIA, USA). The co-solvent used was carbon dioxide (99.9% purity, White Martins, Brazil).

2.3 Transesterification Method

The transesterification reaction of soybean oil with methanol and supercritical CO_2 is represented in the system shown in Figure 2. For the study, the operating conditions were those used in the paper of Han et al. (2005), who also dealt with the supercritical transesterification of soybean oil using methanol. Molar ratios of 1:24 (oil: alcohol) and 0.1 (CO_2 to methanol), rotation of 700 rpm, pressure of 130 bar, temperature of 280 °C and heating rate of approximately 4 °C/min were used. After stabilization of the selected temperature and pressure, the CO_2 inlet valve was opened so that there was no influence of temperature on the system pressure (autogenous pressure). After the reaction time (10 minutes), the sample (Figure 3) was collected and centrifuged (Multifuge X1R-N / S 41464410, ThermoElectron Led GMBH, USA) at 10,000 rpm for 15 minutes to separate the water and glycerin formed.

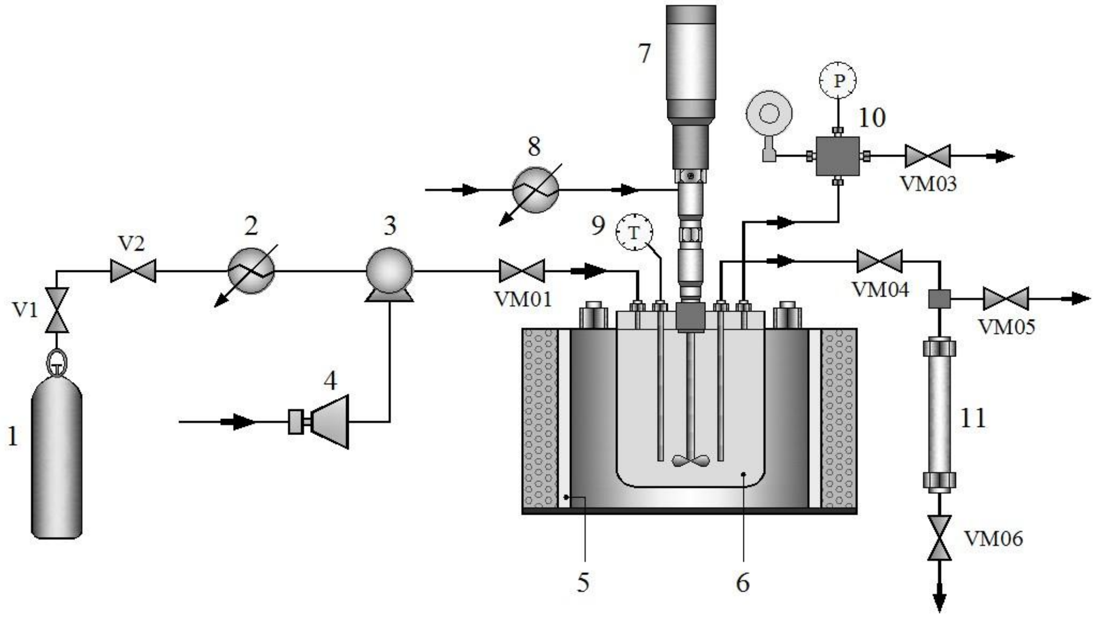

Figure 2. Schematic representation of the system used for methanolic transesterification of soybean oil. 1. CO_2 tank; 2. Cooling bath; 3. Pump; 4. Compressor; 5. Heating collar; 6. Autoclave; 7. Magnetic stirrer; 8. Cooling bath; 9. Thermocouple; 10. Safety head and rupture disc; 11. Sampler; V1-V2 / VM01-VM06 Flow control valves. Described by Bezerra et al. (2018).

2.4 Analysis of the methyl esters obtained

The fatty acid methyl esters were analyzed as described in the literature (Xavier et al., 2011) by gas chromatography-mass spectrometry (GC-MS),using a QP 2010 Shimadzu system equipped with an AOC-20i auto injector, Rtx-5MS silica capillary column (30 m x 0.25 mm, film thickness of 0.25 μm) at temperatures ranging from 100

°C to 280 °C, with a gradient of 4 °C/min and injector temperature of 100 °C; helium as carrier gas at a flow rate of 1.2 mL/min (measured at 100 °C), The injector was of splitless injection, with 0.1 µL of a transesterified solution; programmed temperature of 100°C-280°C with a gradient of 5°C/min. The quadrupole filter scanned from 39 to 550 Daltons once every second. The ionization was acquired by the electron impact technique with energy of 70 eV. Each chemical component was identified by comparing their mass spectra with those in the literature (Adams, 2007) and on the NIST database (Stein, 2011).

2.5 Yield of biodiesel production

The yield of biodiesel production was calculated (Equation 1) based on the fatty acid methyl esters (FAME) analyzed by GC (Baroutian et al., 2010).

$$Yield\ (\%) = \frac{A \times B}{C} \times 100 \qquad (1)$$

Where: *A* is mass of biodiesel produced; *B* is total mass % of FAME; and *C* is mass of oil used in the reaction.

3. Results and Discussion

3.1 Comparison to other studies on supercritical transesterification

Table 1 presents some published works on transesterification by supercritical method.

Table 1. Studies on the transesterification by supercritical method.

Oil	Solvent	T (°C)	P (bar)	τ (min)	MR	Y (%)	Reference
Soybean	Methanol	280	128	10	24:1	98.00	Cao et al. (2005)
Soybean	Methanol	320	320	75	43:1	87.50	Palacios-Nereo et al. (2016)
Castor	Methanol	300	210	90	43:1	96.50	Roman-Figueroa et al. (2016)
Soybean	CO_2	85	80	60	-	92.00	Hu et al. (2015)
Rapeseed	Ethanol	350	120	20	42:1	91.90	Micic et al. (2014)
Castor	Ethanol	350	145	10	40:1	56.20	Rodríguez-Guerrero et al. (2013)

Soybean	Methanol	320	200	40	45:1	92.30	Shin et al. (2013)
Turnip	Ethanol	319	110	22	39:1	97.50	Valle et al. (2010)
Soybean	Methanol	350	150	12,5	40:1	91.40	Wang et al. (2008)
Soybean	Methanol	280	143	10	24:1	98.00	Han et al. (2005)

T: temperature; **P:** pressure; **τ:** time; **MR:** molar ratio; **Y:** esters yield.

The novelty of this work is in the equipment assembly. In fact, it was specifically made with certain specifications required by the authors, for example, inlet and outlet valves for supercritical CO_2, a sampling valve, volume of the autoclave and the maximum pressure and temperature conditions that the reactor would withstand. Therefore, it is not a serial device but an exclusive equipment tailored to the authors's needs. The best conditions of pressure, temperature and molar ratio and the advantages of using methanol were considered from the study of Cao et al. (2005), which was the main paper we made comparisons with.

3.2 Influence of molar ratio

Molar ratio of alcohol to oil is one of the most significant factors that affect the conversion efficiency, yield of biodiesel and production cost (Musa, 2016). Since transesterification is an equilibrium reaction, the excess of methanol was used in order to shift the equilibrium to the right and produce more methyl esters as result of the reaction. Higher molar ratios of methanol to oil also result in a more efficient transesterification reaction, due to the increased contact area between methanol and triacylglycerols (Cao et al., 2005).

Some authors such as Van Kasteren & Nisworo (2007), Baroutian et al. (2010) and Wang et al. (2012) conducted the transesterification reactions using excess alcohol and molar ratio of methanol to oil of 24:1, which was the same proportion used in this work. At this ratio, all of them presented high yields of biodiesel produced (over 90%).

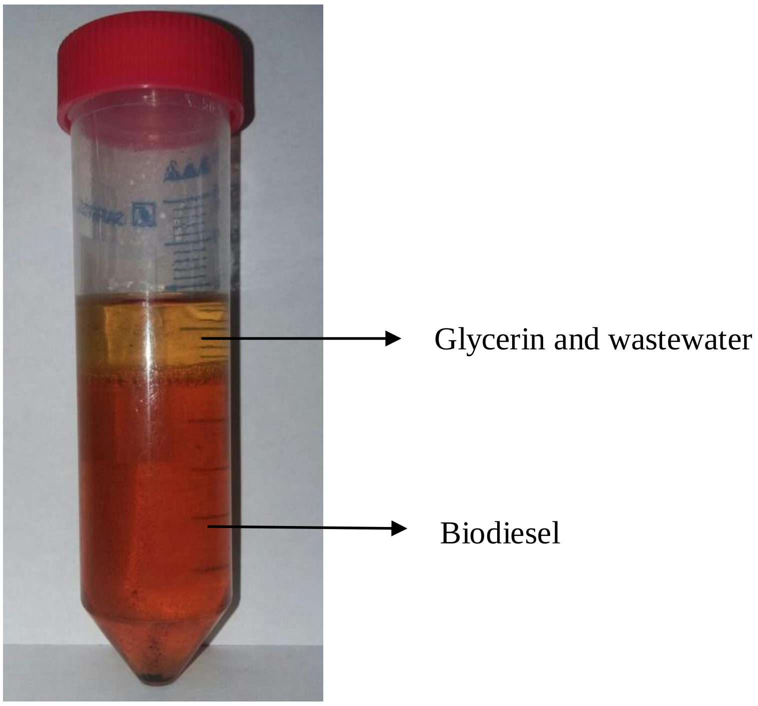

Figure3. ***Sample obtained by supercritical transesterification of soybean oil with methanol and CO_2.***

3.3 Yield of fatty acids methyl esters

In figure 3, it’s possible to see the result of the transesterification process, with a low amount of wastewater and glycerin. The biodiesel yield obtained (Eq. 1) was high and equal to 95.19%, which was close to the results found in the literature. Han et al. (2005) obtained a biodiesel yield of 98%, using the same raw material and operating conditions of this study. Palacios-Nereo et al. (2016) also performed the supercritical transesterification of soybean oil using methanol. They reached yield of 99.9%, at molar ratio 1:42 (oil:methanol), applying gradual heating (0.51 ºC/min), starting from 150 °C up to 320 °C and maintaining this temperature for 10 minutes. They found out that this hybrid process prevented the reactions of thermal decomposition while transforming all triacylglycerols into biodiesel.

According to Shin et al. (2013), in the supercritical transesterification reaction, the purification of products is much simpler, since low amount of unwanted compounds is generated, and high biodiesel yield is reached in a very short time. Thus, the technique with supercritical methanol is considered more economically viable than the use of conventional catalytic reactions.

Regarding the rate of methyl ester conversion, in the sample of oil transesterified with methanol, it is observed (Table 2) that the highest concentration is of linoleate, followed by methyl hexadecanoate, oleic acid methyl ester and methyl stearate with 41.92%, 18.07%, 7.67% and 7.2%, respectively. In general, 10 compounds were identified; together they represent 81.41% of the components present after the transesterification of the soybean oil.

Table 2. Fatty acid methyl esters identified in the transesterified product. Composition obtained by gas chromatography coupled to mass spectrometry

RT(min)	RI	Fatty acid methyl esters	wt (%)
5.325	1114	Methyl octanoate	1.22
11.000	1323	Decadienal<2E,4E->	0.62
26.258	1725	Tetradecanoate<methyl->	1.12
34.017	1945	Methyl hexadecanoate	19.07
35.467	1989	Hexadecanoicacid<n-	0.02
39.100	2102	Linoleate <methyl->	41.92
40.325	2141	Oleic acid methyl ester	7.67
40.675	2153	Methyl stearate	7.2
45.183	2303	11-Eicosenoic acid, methyl ester	1.27
51.483	2531	Docosanoate<methyl->	1.3
Total			81.41

*RT: Retention time; **RI: Retention Index.

In recent article, regarding production of biodiesel from vegetable matrix, Xavier et al. (2011) obtained the compounds methyl hexadecanoate (32%), methyl octadecanoate (29%) and methyl (E)-octadecanoate (29%) of Caryocarvillosum (Aubl.) Pers, in higher concentration after the synthesis with methanol, under normal conditions of temperature and pressure. Of these components, only methyl hexadecanoate was identified in the present work in a lower concentration.

3.4 Comparison to the conventional transesterification method

Wu et al. (2013) performed the conventional transesterification process of soybean oil using methanol and CaO/NaY catalyst. They obtained biodiesel yield of 95% with 30 wt.% of CaO loaded on NaY zeolite, molar ratio 1:9 (soybean oil:methanol), temperature of 65 °C, time of 3 h and catalyst/oil mass ratio of 3%. Liu et al. (2008) also dealt with biodiesel production from soybean oil and methanol, using CaO as a solid base catalyst. Assays at molar ratio 12:1 (methanol to oil), addition of 8% CaO, and 65 ºC gave the best results (over 95%), in 3 h.

In both studies, the biodiesel yield obtained was close to that reached in this work. Despite the fact that lower reaction temperatures and molar ratios were necessary, with no need of increasing pressure, they had to use base catalysts and reaction time was quite superior to that applied in this study. Also, fewer residues are generated, and the product purification is performed in fewer steps. However, it cannot be said that the supercritical transesterification is economically viable compared to the conventional technique, due to energy and equipment costs are higher than those observed in a conventional process. Thus, a comparative economic analysis is necessary.

3.5 Influence of the reactor type used in the transesterification process

Silva and Oliveira (2014) state that the biodiesel production under supercritical conditions requires high processing costs (high molar ratios, pressures and temperatures) and some strategies to reduce the expected high operating costs usually involve the addition of co-solvents and the use of different reactor configurations with increased mass transfer, operating in continuous mode (microreactor or packed bed reactor). Many authors such as Pohar and Plazl, 2008; Hessel et al., 2005 and Wen et al., 2009 recommend to conduct transesterification reactions in microreactors in order to reduce the limitations of mass and heat transfer, since such parameters tend to increase due to the small size and large contact area (Pohar and Plazl, 2008), and the small internal diameters (typically 10-300 μm) promote interaction with the reagents at molecular level. In the case of the reactor used in this study, its internal diameter (51 mm) and volume (0.095 L) represent the most suitable configuration, which was verified by the high biodiesel yield obtained (95.19 %).

Comparing to other studies, Wang et al. (2008), for example, used a continuous tubular reactor with no mechanical blending to perform the transesterification reaction of soybean oil with methanol under supercritical conditions. Thus, in order to increase the biodiesel yield, they had to acidify the soybean oil by adding a certain amount of organic into the reaction system. At the molar ratio of 1:20 (oil:methanol), the biodiesel yield of acidified oil, and non-acidified oil were 82.3 and 60.0%, respectively.

4. Conclusion

The reactor used in this study proved to be efficient for the transesterification process. The reaction time was only 10 minutes, under experimental conditions of 130 bar, 280 ºC and molar ratio of raw material to methanol of 1:24, and CO_2 to methanol of 0.1. The yield of biodiesel was 95.19% and the yield of methyl esters was 81.41%, with linoleate being the compound found in the highest concentration. The results indicate that the undesirable compounds glycerin and wastewater were obtained in low concentrations, which means that this method can be applied to obtain biodiesel with no need of base catalysts and fewer steps of purification compared to the conventional method.

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Appendix

EQUIPMENT DESCRIPTION

5. AUTOCLAVE CHARACTERISTICS

5.1 Technical datasheet and marking

Table 3 shows specifications such as brand, model, size and operating range of pressure and temperature.

Table 3. Autoclave characteristics

Manufacturer	Top Industrie
Description	Autoclave
Type	Autoclave (2777 1000)
	Off Category according to PED 97/23 ($v < 0,1$ L)
	Serial Number - 2986
Year of Manufacture	2015
Production Site	FR – 77 013 VAUX LE PENIL
Selected design method	CODAP 2005 Division 2 + Rev. 09/07 and 03/09
Evaluation procedure	A Module
Dimensions	Ø 128 x 152 mm
Internal Volume (V)	0,095 L
Operating Pressure (PU)	300 bar
Maximum Allowable	400 bar

Pressure (PS)		
Pressure Test (PT)	667 bar	
Operating Temperature (TU)	10 °C to 350 °C	
Design Temperature (TS)	10 °C to 400 °C	
Material		**Drawing**
	Body: 1.4571 according to NF EN 10272	2777 1020
	Plate: 1.4571 according to NF EN 10272	2777 1013
	Ring: 1.4980 according to NF EN 10269	2777 1012
	Nut: 1.4980 according to NF EN 10269	2777 1010
Type of fluid	Group 1	

5.2 General characteristics:

Figure 4 shows the autoclave in its structural frame coupled to the gas supply system and stirrer with water for its cooling system. Table 4 shows the dimensions of the structure with the autoclave.

Figure 4. ***Frame with autoclave***

Table 4. Measures of the frame with autoclave

Magnitude	Approximatesize
Width(mm)*	510
Height(mm)	850
Depth (mm)	420

*(not including the 4 ground fixing squares)

6. DESIGN

6.1 Control cabinet

From the control cabinet (Figure 5), it’s possible to do:i. reading and regulation of the stirring speed; ii. temperature reading and regulation; iii. pressure reading; iv. flow measurement; v. emergency stop button.

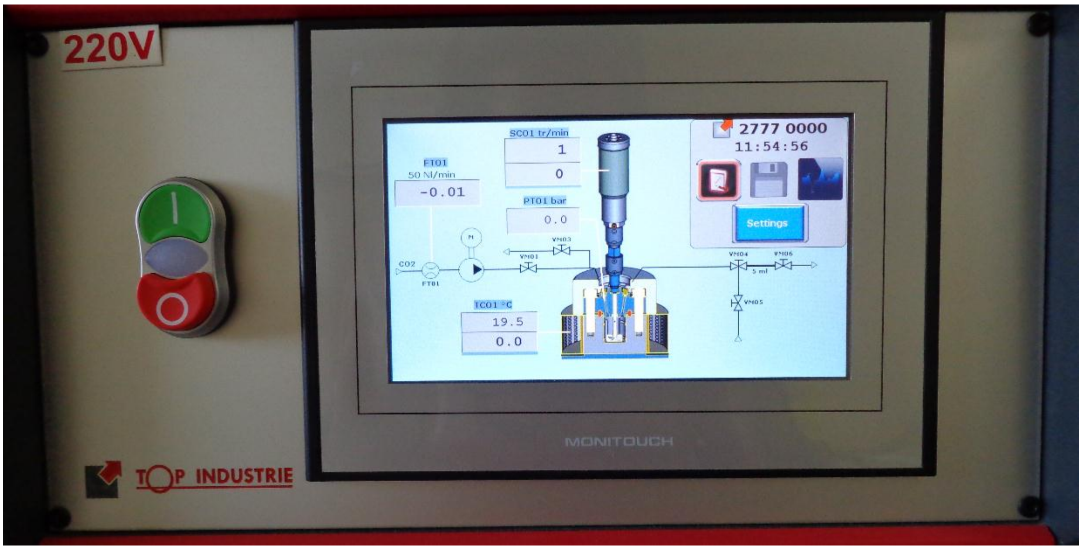


*Figure 5. **Control cabinet***

The control cabinet has the following features:

- Electrical supply: 230 VAC / 50-60 Hz / 16 A
- Maximum power: 3000 W

7. ASSEMBLY OF THE AUTOCLAVE:

For correct assembly of the autoclave it is necessary to perform the following procedures:

- Check the property of the surfaces receiving the seal;
- Pull of the seal and clean it;

- Check the property of the threads on the body and the ring;
- Put if possible high temperature grease on the threads;
- The liquid should never completely fill the autoclave;
- Close the autoclave and tighten with the torque wrench showed in Figure 6 (Facom/nS.306A100 + extension S.210 + socket Hex 24mm S.24H), in cross with tightening torque 20 N.m, then tightening torque 50 N.m (see Figure 7 for the detail of tightening in cross);
- Make if possible a tightness test at room temperature;
- Mount the insulating mantle on the top of the autoclave.

Figure 6. ***Torque wrench to close the autoclave***

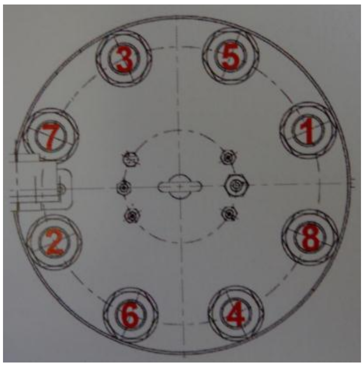


Figure 7. ***Detail of tightening in cross to correctly close the autoclave***

<u>Observation:</u> Never scratch contact surfaces from body or plate with a metal object, above all the effective cover area of gaskets. Never loosen or tighten up connections under pressure.

8. OPERATING OF THE AUTOCLAVE AND CONTROL CABINET - STANDARD OPERATING PROCEDURES (SOP'S)

8.1 Detailsofthe autoclave

The figure 8 shows the location of the pressure transmitter, the safety head and disc, the manual valves, the mechanical boy and the floor fixing squares.

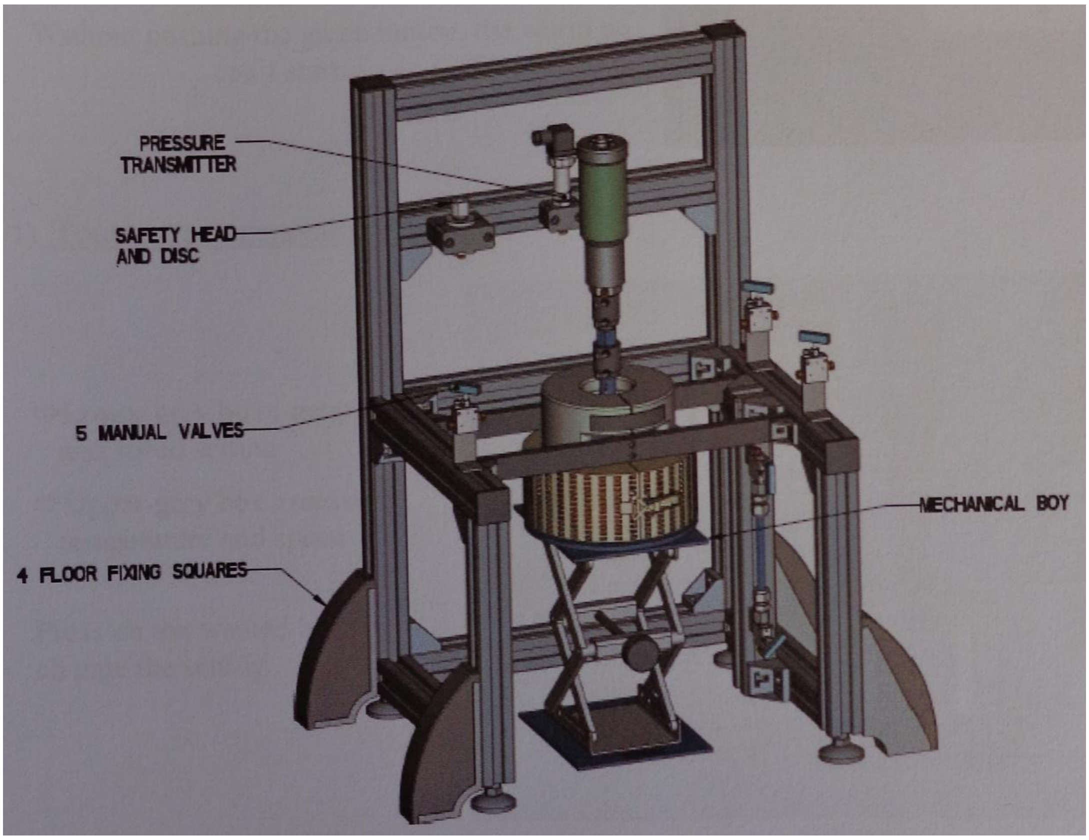


Figure 8. ***Details of the autoclave***

8.2 Use of the control cabinet

To use the control cabinet is required:i. powering of box by the master switch on the rear side (Figure 9.a); ii. start of the general by the green button "I" (Figure 9.b) without pushing the green button, the warm up can´t start.

Figure 9. ***Parte traseira (a) e parte frontal do controlcabinet (b)***

8.2.1 Touchscreen general screen

The screen presents two main boxes for controlling of temperature and speed (Figure 10):

- Upper-grey box: measured temperature and speed. It's necessary to press on the wanted box no change the settings ("A.1");
- Lower grey box: temperature and speed setting ("A.2").

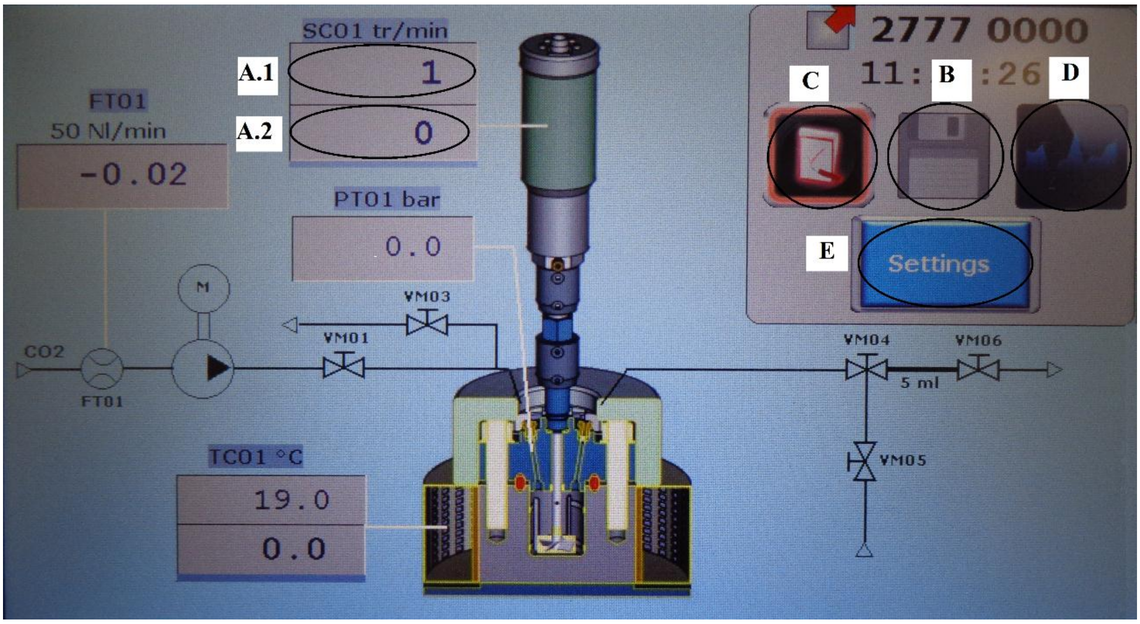


Figure 10. ***Touchscreen cabinet control***

Notes:

- To save the data, insert the USB key before the beginning of test to begin the recording of the test data (USB connection beside the box) – No data storage without USB key.

- Press on “B” (Figure 11) to start the recording of the temperature value;
- Press on “C” (Figure 11) to go to the “ Warring screen”;
- Press on “D” (Figure 11) to go to the “Curves screen”.

8.2.2 Setting Screen

Press on the “Settings” (Figure 11 - “E”) on the general screen:

- Press on the wanted box to have access to the HOUR screen (Figure 11 – “A”);
- Modify the values with the boxes “+” and “-”, then validate on “B” and go back to the general screen by pressing on “C” (Figure 11).

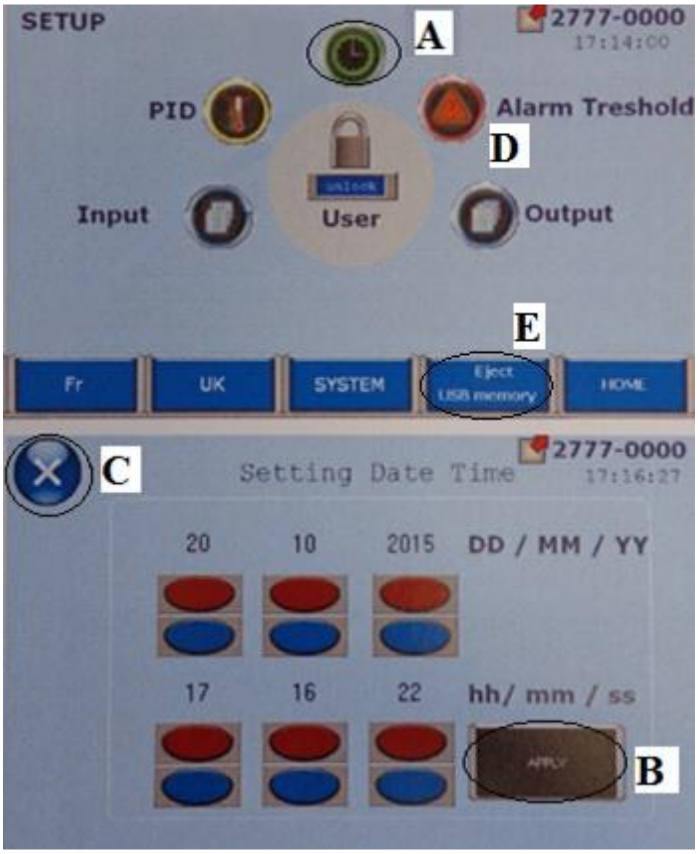
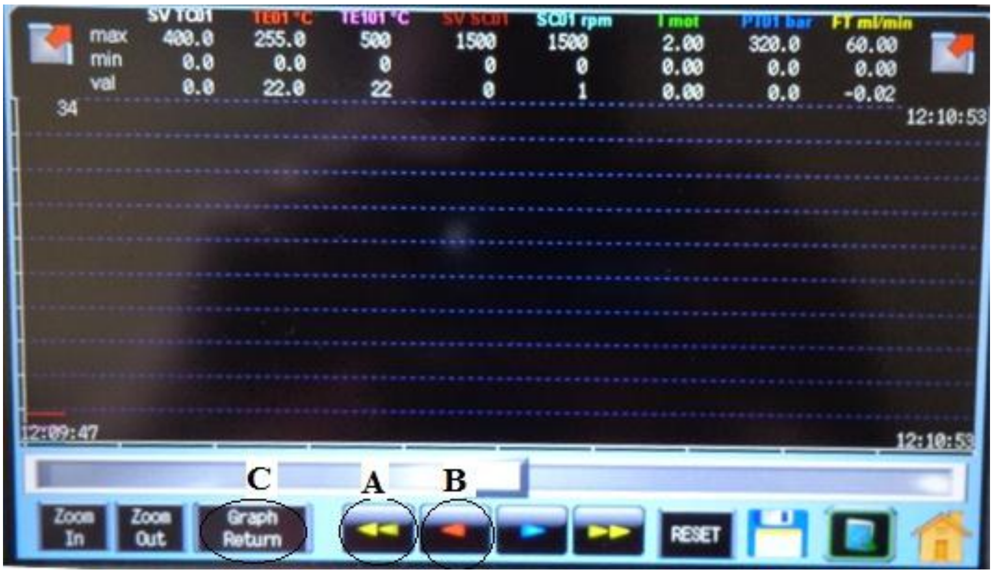


Figure 11. ***Modifying some settings***

8.2.3 Curves screen:

To go to curved screen is necessary to press the "D" icon (Figure 11).

- In the graphic boxes press on the icons “A” for 30 seconds, return to box and press on “B” for 5 seconds and return (Figure 12);
- Press the icon “Graph return” – “C” (Figure 12) to return at real-time;
- To change the scale of the Min or Max values: i. press on the value to change; ii. enter the new value on the keyboard; iii. validate by “OK”.



	SV TC01	TE01 °C	TE101 °C	SV SC01	SC01 rpm	I mot	PT01 bar	FT ml/min
max	400.0	255.0	500	1500	1500	2.00	320.0	60.00
min	0.0	0.0	0	0	0	0.00	0.0	0.00
val	0.0	22.0	22	0	1	0.00	0.0	-0.02

Figure 12. ***Curves screen***

8.2.4 Ejection of the USB key at the end of the test to get back the test curves:

- Press on “Eject USB Memory” (Figure 11 – “E”) and wait for the flickering of the paving stone.
- Storage of the data in the file DA T0000\SAMPLES\SMP0000.csv

<u>Note:</u> the ejection of the USB key stops the posting of the curves on the screen

8.2.5 Warning screen

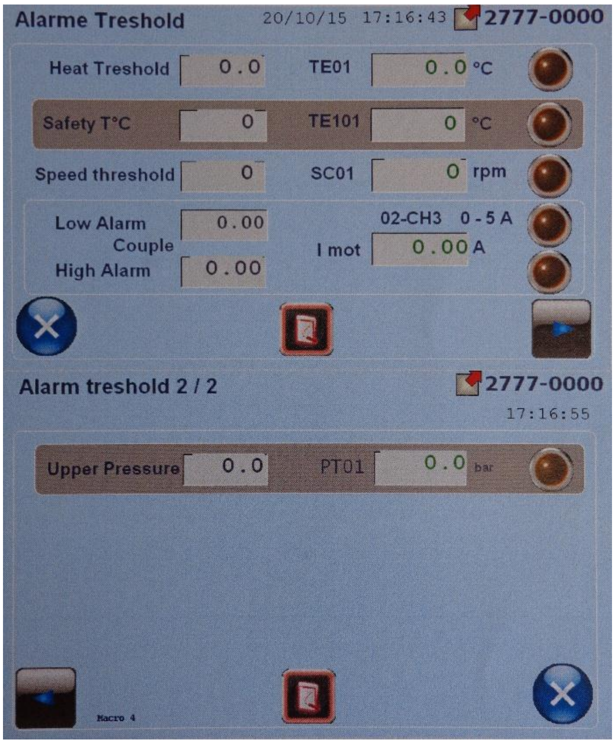
Press on “C” (Figure 11) to reach the screen. In this screen (Figure 13) you see information about alarm, alarm list, hours of start hour of ending. If the hour of ending is not written, the alarm is still continuing.

Figure 13. **Warning screen**

8.2.6 *Alarm Threshold*

To access this function press on the settings screen (Figure 11 - “D”) to reach this screen (Figure 14).

In this screen you can put alarm on different temperatures (right box in green) and measured temperatures (left box in blue).


Alarme Treshold 20/10/15 17:16:43 2777-0000

Heat Treshold 0.0 TE01 0.0 °C

Safety T°C 0 TE101 0 °C

Speed threshold 0 SC01 0 rpm

Low Alarm 0.00 02-CH3 0 - 5 A

Couple I mot 0.00 A

High Alarm 0.00

Alarm treshold 2 / 2 2777-0000 17:16:55

Upper Pressure 0.0 PT01 0.0 bar

Figure 14. **Alarm Threshold**

9. MAINTENANCE

9.1 Principles for high pressure parts:

- *Pipe connections:*
  - *Make sure that the connection is equivalent to the desired pressure;*
  - *Increase pressure by stages and check the mechanical resistance;*
  - *Never look for a leak using the hands;*
  - *Never stand in front of a connection which has just been made;*
  - *All connections shall be tested at maximum operating pressure before normal operation.*
- *Put a plug on all openings not used (circuit cleanliness).*
- *All used connections shall be referenced showing the operating pressure.*
- *List the internal connections;*
- *All connecting capillary tubes shall be fitted with a whiplash prevention system.*

9.2 Autoclave 2777 1000:

Before carrying out maintenance, each time check that appliance is at ambient temperature and zero pressure using the pressure and temperature sensors located on the appliance.

9.2.1 Annual preventive maintenance:

- Check the inside and outside parts under pressure to look for any damage or signs of corrosion.
- Check the safety organ (we recommend to change the safety disc).
- Check the pressure transmitter and the temperature measure loop.

9.2.2 Corrective maintenance:

- Check the gasket faces in the autoclave in the event of a leak, and stripe impose a machining repairing.

9.3 Maintenance expected for spare parts:

The designation, size, supplier and use of spare parts are shown in the table 5.

Table 5. Spare parts

Unit	Designation	P/N	Supplier	Use
2	O-ring viton	Ø 10,82 x 1,78	Sephat or equiv.	Stirrer internal
2	O-ring viton	Ø 14 x 1,78	Sephat or equiv.	Stirrer internal
3	Bearing	604 01 40 1192N	TOP INDUSTRIE	Stirrer internal
2	O-ring	2659 2005	TOP INDUSTRIE	Stirrer/autoclave
2	Plate seal	R 18 OCTOGONAL -POUR BRIDE RT	DELTA FLUIDE	Autoclave seal
4	O'ring Viton	Ø 20,35 X 1,78	Sephat or equiv.	Water jacket seal

9.4 Stirrer series 618 01 00

9.4.1 Bearings

- If the stirrer becomes noisy and/or vibrates, the bearings must be changed.
- If the noise and/or the vibrations persist, the stirrer must be returned to our after-sales service.
- The transversal groove on the bearing must not be in contact with the encapsulation.

9.4.2 Monthly preventive tightness maintenance

- O-ring seal marker 8: if the ‘O’ ring seal marker 8 is faulty, the gas leak will be canalized into the leak hole of the distance sleeve marker 2 (Figure 15). Use a bubbling product (water and soap) to control whether the O-ring is perfectly thight/fitting;
- Seal (between part marker 2 and flat bottom): Use a bubbling product (water and soap) directly on the connection (M20 x 150) between the stirrer and the autoclave head (Figure 15);
- Motor, ball bearing, magnetic coupling: no maintenance. If a problem appears, the complete stirrer must be returned to our after-sales service.

9.4.3 Annual preventive maintenance

- Change the bearing and the O-ring;

- Check the magnetic coupling efficiency;
- For maximum protection, the stirrers are designed so that the compressed air or electric motor blocks and not the magnetic coupling.

9.4.4 Corrective maintenance

- If the stirrer becomes too noisy or vibrate, change the bearings;
- If the noise still exists, the stirrer must be returned to the SAV service for repairing.

Corrosion: The parts that are in contact with the fluid are made of stainless steel 1.4404 and 1.4980. No traces of corrosion should appear. If this were to happen, it would be because the equipment was not suitable for application. It is dangerous and forbidden to use a stirrer under such conditions.

9.4.5 Dismounting

- Disconnect the stirrer from its power or energy supply;
- Disconnect the stirrer from the autoclave;
- Unscrew and remove the screw marker 6 (Figure 15);
- Unscrew the motor-distance sleeve (marker 12) while holding the body (marker 2) and the ring marker 9; apply pressure slightly in order to defeat the attraction of the magnetic field (Figure 15);
- Unscrew the ring number 9 while holding the body marker 12 (Figure 15);
- Pull the upper body marker 11 towards the top. Remove the stirring module;
- The central axis marker 9 (Figure 15) may now be removed from its housing;
- The bearings (marker 1) and the O-ring (marker 8) are now accessible for checking or replacement (Figure 15).

9.4.6 Assembly

After having thoroughly cleaned all the parts and having, if necessary, proceeded to replace the bearings marker 1 and the seal marker 8 (Figure 15), reassemble as follows:

- Slide the central axis marker 9 (Figure 15) into its housing and manually, make sure that the it rotates correctly;

- Put marker 11 (Figure 15) back into place by forcing slightly. If permitted, it is advisable to apply a drop of lubricant such as vaseline in order to make sliding easier on the joint;
- Manually screw back on the part marker 12 (Figure 15). Tighten until metal against metal contact is obtained;
- Rescrew the screw marker 6 (Figure 15).

Note: for the P/N of the bearings and O'ring, see the autoclave part list

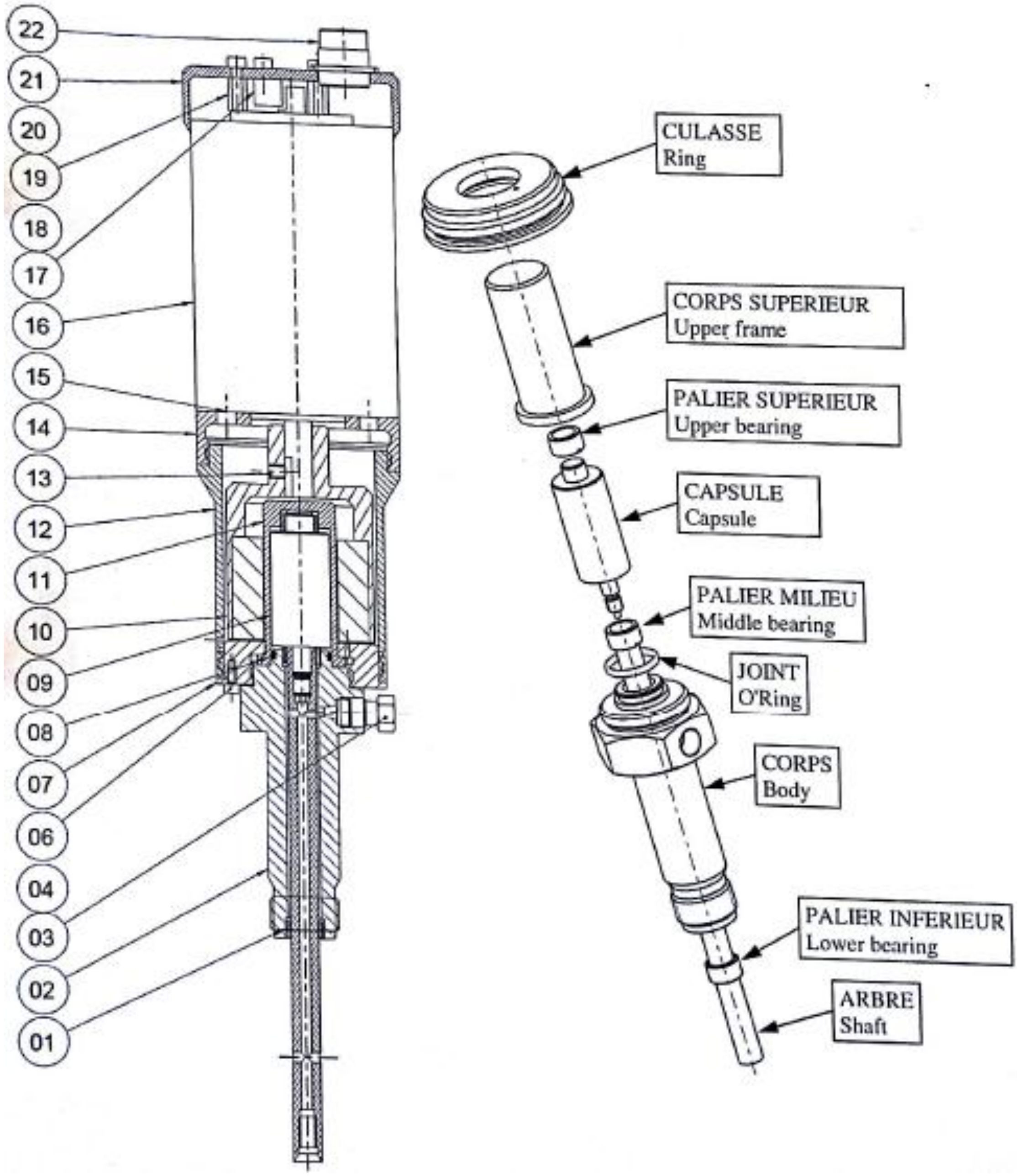


Figure 15. ***Stirrer's parts***

Settings of parameters on the touchscreen:

Accessible by pressing on the button *Settings* (Figure 11 - “E”). The settings are locked by default (“lock”). To unlock, press on the ‘unlock’ box (Figure 16 – “A”); when the next screen appears, enter the password (TOP) and validate by “Enter” and press on “B” (Figure 16) to go back to the *Setting screen*.

<u>Note</u>: Any parameter modification must be made only by qualified person.

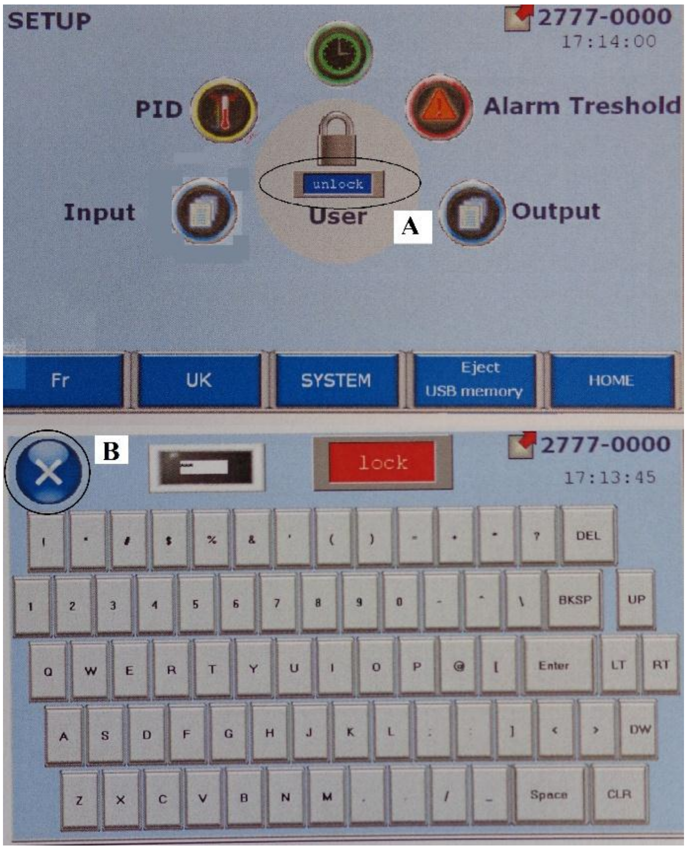


Figure 1. ***Unlocking the settings***

Technical data

Electrical characteristics

Power supply voltage Vcc (tolerated ripple $<$ 5% ………………………..10 to 60 DVC
Permanent output current I_{mom}…………………………………………………10 A
The motor current is limited to I_{mom} + I_{boost} for 500ms then to $I_{mom}$for 10s (motor overload) before being cut (motor locks up). Any current return under the limitation resets the detection time
Commutation frequency………………………………………………………. 20 KHz

Inputs

SET VALUE: Set point value (terminals 1, 2 and 3)………...**0/+10 DVC** ($R_t >$ 10 KΩ)
ENABLE: active when the contact is closed (terminals 4 and 8)……......... **Dry contact**
CW/CCW: open contact: clockwise (terminals 5 and 8) contact closed:
Counterclockwise direction…………………………………………………**Dry contact**
In the event of an inversion of the rotation direction with a non-zero speed, the servo amplifier waits until the current is cancelled in the motor before reversing the rotation direction.

Outputs

I MOT: Image with I_{mom} current voltage during nominal operation (terminals 9 & 12)
This output is protected against short-circuits………………...**0/ + 10 VDC** (R_0 = 100Ω)
Proportionality factor…………………………………………………………**1V/2A**
MONITOR: Image with I_{mom} and I_{boost}current voltages during settings (terminals 10 & 12)
This output is protected against short-circuits…………………**0/ + 5 VDC** (R_0 = 100Ω)
Proportionality factor…………………………………………………………**1V/2A**
READY: Message for monitoring the state of card (terminals 11 and 12)
Open collector not protected from the short-circuits………..**max. 30 VDC** ($I_t <$ 20 mA)

Output voltage

+ 10V: Auxiliary voltage (terminals 1 & 3) ……………………**+10 VDC,** max. 20 mA
Protected against short-circuits and overloads

Setting Push buttons

OK: Validation or setting mode input/output
+ : Increase of parameterisable values
+ : Reduction of parameterisable values

LED indicador

Green LED……………………………………………………...Presence of voltage
Orange LED Steady………………………………………...Clockwise rotation direction
Orange flashing LED………………………………Counterclockwise rotation direction
Red LED…………………………………………………………………………Fault

Temperature / Humidity

Operation…………………………………………………………………..**0 to +45°C**
Storage……………………………………………………………………..**-40 to + 85°C**
Relative humidity……………………………………………**20 to 80% non-condensed**

Mechanical characteristics

Weight………………………………………………………………..**approximately 220 g**
Dimensions……………………………………………..**102 x 100 x 32 (or 3U frame)**
Mounting plate………………………………………………………………..**for M4 screw**

Connections

Terminals with screws**………………………………….”Power”(4 poles), “Signal”(12 poles)**
Power step………………………………………………………………………**5.08 mm**
Suitable for sections of wire……………………………………………**0.5 to 2.5 mm^2**
Signal step………………………………………………………………………**3.81 mm**
Suitable for sections of wire……………………………………………..**0.14 to 1.5 mm^2**

The table 6 shows the parts list as well as their material and suppliers.

Table 6. Parts list

PARTS LIST

TOP INDUSTRIE
AUTOCLAVE
2777 1000

Rep	*Nb*	*DESIGNATION*	*MATERIAL*	*Ref.Top*	*Ind.*	*Ref. SUPPLIER*	*SUPPLIER*
01	1	MAGNETIC STITRRER 30 N.cm		616 01 00	D		TOP INDUSTRIE
02	2	WATER JACKET		604 99 00	C		TOP INDUSTRIE
03	1	STIRRER ADAPTER	1.4404	269 1004			TOP INDUSTRIE
04	1	STIRRER SEAL	VITON			Ø10,82x1,78	SEPHAT
05	4	1/8” HP SCREW		920 01 00			TOP INDUSTRIE
06	4	1/8” HP FERRULE		920 02 00			TOP INDUSTRIE
07	1	MANTILE INSULATOR		2777 1007	A		TOP INDUSTRIE
08	1	STIRRER SEAL WASHER	1.4404	2777 1008			TOP INDUSTRIE
09	1	STIRRER SEAL	NIKEL	2659 2005	A		TOP INDUSTRIE

10	8	NUT - M16 x 1,5	1.4980	2777 1010			TOP INDUSTRIE
11	8	WASHER M16	INCO 718	692 02 16 INCO 718			TOP INDUSTRIE
12	8	STUD – M16	1.4980	2777 1012			TOP INDUSTRIE
13	1	FLAT BOTTOM	1.4571	2777 1013			TOP INDUSTRIE
14	1	FLAT SEAL	STAINLESS STELL			R 18 OCTOGONAL RTJ FLANGE	TOP INDUSTRIE
15	2	LOWER BEARING	1192N	604 01 40	B		TOP INDUSTRIE
16	1	Hc M3 X 8 mm SCREW				Hc M3 X 8	TOP INDUSTRIE
17	1	DB BAFFLE BAR	1.4404	**653 00 DB 00**			TOP INDUSTRIE
18	1	STIRRING SHAFT	1.4404	2777 10 18			TOP INDUSTRIE
19	1	ø20 IMPELLER		**608 01 94 00**			TOP INDUSTRIE
	1	BODY IMPELLER	1.4404	**608 01 94 01**			TOP INDUSTRIE
	8	BAR	1.4404	**608 01 94 02**			TOP INDUSTRIE
20	1	BODY	1.4571	2777 10 20			TOP INDUSTRIE
21	1	HEATING COLLAR		2777 10 21			TOP INDUSTRIE
22	2	FHc M8 x 25 mm (HIGH TEMPERATURE) SCREW	STAINLESS STELL			Fhc MB x 25	BAFA
23	1	BOTTON INSULATOR	MICA SILICONE	2777 10 23	A		TOP INDUSTRIE
24	1	THERMOCOUPLE K ø1,5 – L 200 mm				TKA 15 x 20 HMP	ERCIAT
25	1	THERMOWELL	1.4404	2777 10 23			TOP INDUSTRIE
26							
27		**<u>PIECES DE RECHANCE</u>**					
28	2	STIRRER SEAL	VITON			ø10,82x1,78	SEPHAT or equiv.
29	2	STIRRER SEAL	NIQUEL	2659 2005	A		TOP INDUSTRIE
30	9	BOTTON FLAT	INOX			R 18	DELTA

		SEAL				OCTOGONAL RTJ FLANGE	FLUIDE
31	3	LOWER BEARING	1192N	604 01 40	8		TOP INDUSTRIE
32	1	TORQUE KEY (50 N.m)				S.308 A 100	FACOM
33	1	RATCHET				S.210	FACOM
34	1	HEXAGONAL SOCKET M 16 / HEX 24 mm				S.24H	FACOM
35	3	LOWER BEARING	Graphite	**604 01 40 GR**	B		TOP INDUSTRIE
36		O'RING (INTERNAL STIRRER)	VITON			Ø14 x1,78	SEPHAT or equiv.
37		O'RING (WATER JACKET)	VITON			Ø20,35x1,78	SEPHAT or equiv.

CAPÍTULO 5

OBTENÇÃO E TRANSESTERIFICAÇÃO SUPERCRÍTICA DO ÓLEO DE RESÍDUO DE PALMISTE INDUSTRIAL: ARTIGO INTITULADO “Supercritical CO_2 Extraction and Transesterification of the Residual Oil from Industrial Palm Kernel Cake with Supercritical Methanol”

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Abstract

The oil extracts from palm kernel cake were obtained with supercritical CO2 at temperatures of (40 to 80) °C and pressures of (150 to 350) bar. The highest extraction yield on dry basis was (7.82 ± 0.28) %, obtained at 350 bar/80 °C; however, the oil fraction employed in the transesterification process was that obtained at 150 bar/40 °C. The transesterification reaction was performed under the following operating conditions: methanol/oil molar ratios of 24:1 and 42:1, temperatures of (250 to 350) °C, and reaction times of (5 to 25) min. A statistical analysis and mathematical modeling for the optimal yield of SFE were also performed. The fatty acid with the highest concentration was lauric acid (60.24 ± 0.62) % and the transesterification conditions affording the highest conversion of methyl esters (99.81 ± 0.10) % were a methanol/oil molar ratio of 42:1, 350 °C, and 5 min.

Keywords: Industrial residue, Supercritical fluid, Methyl esters, Extraction, Biodiesel

1. Introduction

Nowadays, vegetable oils represent the major products extracted from plants. The consumption of vegetable oils has increased worldwide, taking over part of the animal fat market. Most of these oils are used in industrial processes as well as in human and animal food. As a result of the increased consumption, their production has also increased, which can be carried out using various plant species.

One of these species is palm (Elaeis guineensis Jacq.), which is assumed to be originally from Africa and provides two types of oil: palm oil, extracted from the mesocarp, and palm kernel oil (PKO), obtained from the kernel. The kernel consists of layers of oily endosperm surrounded by a network of fibers, which has great commercial value as raw material for the food, chemical, and cosmetics industries [1,2].

Palm kernel cake (PKC) is obtained from the palm oil extraction process. Its production in 2017 reached over 9.6 × 106 ton worldwide [3]. One of the most important uses of this residue is in animal feed owing to its high protein and fiber content. It can also be used as an energy source for boilers, re-extraction, etc. Palm kernels contain about 45 % to 50 % of oil on wet basis; after mechanical extraction, they may still contain up to 12 % of oil, which can be recovered by solvent extraction. The Soxhlet method, for instance, uses organic solvents; however, it suffers from many drawbacks such as environmental pollution, contamination of the extracts, high energy consumption, and high cost [4–9, 50].

In order to avoid these problems, supercritical fluid extraction (SFE) has been developed as a “green” alternative processing method that can extract natural products including fats and oils with high quality and purity. Therefore, SFE is also an important process in the food, pharmaceutical, and cosmetics industries. The most commonly used solvent for SFE is carbon dioxide (CO2), whose low critical temperature and pressure (31.1 °C and 72.8 bar, respectively) make it an ideal solvent for the extraction of thermally sensitive compounds. This solvent is also non-toxic, non-flammable, and environmentally acceptable [10–13, 47]. As a result, SFE represents an important method to recover the remaining oil present in the PKC obtained from industrial processes. Recently, Hossain et al. [9] have investigated the palm kernel residue from a screw press process and achieved a yield of 9.26 % at 70 °C and 41.76 MPa.

One of the applications of palm kernel is in the production of biofuels. Bioethanol was produced by Cerveró et al. [14] by fermentation of the carbohydrates present in this residue. Another biofuel that can be produced is biodiesel, which comprises monoalkyl esters resulting from the reaction of long-chain fatty acids with a short-chain alcohol. Many researchers have studied the production of biodiesel from PKO [15–23].

In particular, using the supercritical method of PKO transesterification with methanol, Bunyakiat et al. (2006) [57] achieved a methyl ester conversion of 96 % at an oil/methanol molar ratio of 1:42, 350 °C, and 19 MPa. Likewise, Sawangkeaw et al. [24] obtained 93.7 % of alkyl ester conversion at the same oil/methanol molar ratio, 325 °C, and 18 MPa.

Such a process presents important advantages over conventional catalytic biodiesel production: it tolerates certain amounts of water and free fatty acids, affords high reaction rates without a catalyst, and enables shorter reaction times with simpler purification and separation steps [25–29].

In this context, the aims of this study were to characterize the PKC, obtain oil extracts by Soxhlet (using hexane as the solvent) and SFE (at different supercritical conditions with CO2 as the solvent) methods, analyze the product chemical composition, compare the two techniques and, differently from other studies on palm kernel oil, use, for the first time, the oil obtained by SFE at 40 ºC and 150 bar for transesterification with supercritical methanol. In this way, the palm kernel residue can be completely repurposed. Also, a statistical analysis and mathematical modeling for the optimal yield of SFE were also performed.

2. Materials and Methods

2.1 Preparation and characterization of the raw material

The PKC was donated by Agropalma S.A. (Tailândia, Pará, Brazil) on July 16, 2015. It was dried in an air-forced circulation oven (FABBE, model 170, Brazil) at 60 °C for 24 h. Then, the sample was ground in a knife mill (Tecnal, model TE-631/3, Brazil) for 15 s. The true density of the particles was determined using a helium pycnometer (Quantachrome, model Ultrapyc 1200e, USA). The apparent bed density was calculated using its volume and the mass of the sample deposited on it. The total porosity was determined from the values of the real and apparent densities.

The analysis of the moisture content, total protein, ash content, total lipid concentration, and crude fibers was performed before and after SFE. The carbohydrate content was determined by difference (100 minus the sum of the other values). The moisture content was determined by distillation with xylol (Ecibra, PA-ACS, São Paulo, Brazil) [30]. The total protein content was determined using the Kjeldahl method and the ash content by the dry-ashing method at 550 °C for 6 h [31]. The total lipid concentration was determined by ether extraction using petroleum ether (Dinâmica, PA-ACS, Brazil) at approximately 50 °C in a Soxhlet apparatus [32] and the crude fiber content was determined by the Van Soest [33] method. The experiments were performed in triplicate.

2.2 Extraction procedures: SFE and Soxhlet methods

Supercritical fluid extraction was performed using a Spe-ed^{TM} SFE system (model 7071, Applied Separations, Allentown, PA, USA). The global yield isotherms were determined using 0.022 kg of the ground sample. The temperatures applied were 40 °C, 60 °C, and 80 °C and pressures of 150 bar, 250 bar, and 350 bar. The solvent used was CO_2 (99.9 % purity, White Martins, Pará, Brazil) with a constant mass flow rate equal to 8.85×10^{-5} kg/s. The assays were performed in triplicate. The extraction time was 1800 s in batch operation and 7200 s in semi-continuous operation. The supercritical CO_2 density was estimated using the software TermoDi, which applies the Peng–Robinson [34] cubic equation of state developed by the Laboratory of Physical Separations of the University of Campinas (São Paulo, Brazil). The extraction unit is shown in Figure 1.

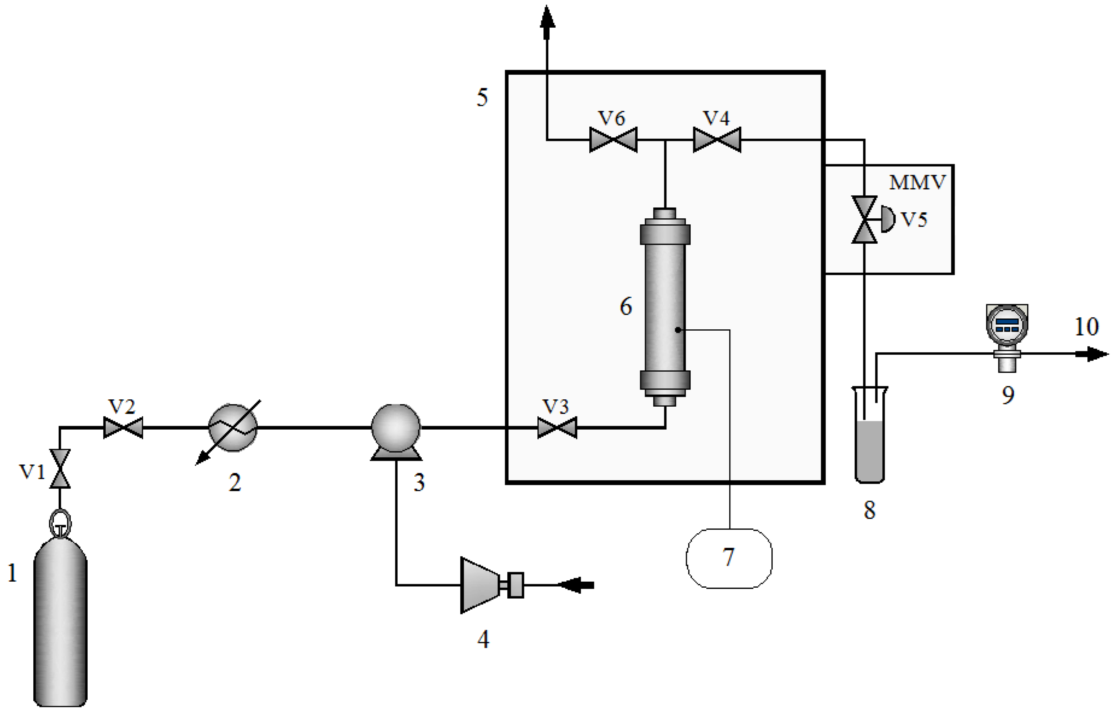


Figure 01. SFE extraction unit. 1. CO_2 tank; 2. Cooling bath; 3. Pump; 4. Compressor; 5. Oven; 6. Extractor vessel; 7. Monitor; 8. Vial; 9. Flowmeter; 10. CO_2 Outlet; V1 – V6 Flow control valves [37]

Soxhlet extraction experiments were conducted for comparison purposes and carried out in duplicate. A solute/solvent ratio of 1:10 (in weight) was employed, according to the methodology proposed by Instituto Adolfo Lutz [35]. Approximately 11 g of the sample and 110 mL of hexane (65.0% purity, Vetec, Brazil) were used. The mixture was refluxed for 5 h in a 250 mL Soxhlet apparatus. Hexane was removed by evaporation in an oven at 101 °C for 2 h.

The global yield of both techniques was determined as the relationship between the oil mass obtained and the initial mass of PKC used for extraction in dry basis (db) [30], according to equation (1). An analysis of variance (ANOVA) and Tukey test at 95% confidence level were performed using the software STATISTIC 7.0 (StatSoft, Inc., Oklahoma, EUA).

$$X_{0_{db}}\ (\%) = \frac{m_o}{m_s \cdot \left(1 - \frac{M_s}{100}\right)}\ x\ 100 \tag{1}$$

Where $X_{0_{db}}$ is the yield on dry basis, m_o is the oil mass, m_s is the sample mass and M_s is the sample moisture.

2.3 Fatty acid content in oil extracts

The fatty acid contents in the extracts obtained by the SFE and Soxhlet methods were determined according to the methodology suggested by Hartman and Lago [63]. The analyses were performed by gas chromatography (model 6820 BPX90, Agilent, USA) equipped with a flame ionization detector and a capillary column (DB23, Agilent, USA; 60 m long × 0.25 mm internal diameter × 0.25 µm film thickness). Hydrogen was selected as the carrier gas at a flow rate of 1.0 mL/min, with a flame ionization detector at 250 °C and an injector at 280 °C. The temperature of the column was set to 70 °C for 4 min and then increased to 250 °C at a rate of 5 °C/min. The fatty acid peaks were identified by comparing the retention times with those of standard fatty acids (Nu-check-prep, Inc., USA) using the software Agilent Cerity. The experiments were performed in duplicate.

2.4 Transesterification using supercritical methanol

To perform the transesterification process, an autoclave (model 2777 1000, Top Industrie, France) with an internal volume of 0.095 L was employed, as described by Bezerra et al. [37], coupled to an air compressor (model CSA, Schulz S/A, Brazil), a CO_2 cylinder, and a recirculator (model F08400796, Polyscience, USA). The oil obtained at 40 °C/150 bar was introduced in the reactor with methanol (Isofar, PA-ACS Ref. 0203, Brazil) and CO_2 (99.9 % purity, White Martins, Brazil). The methanol/oil molar ratios used were 24:1 and 42:1, at temperatures of 250 °C, 300 °C, and 350 °C, CO_2 mass of 6×10^{-7} g, pressure of 200 bar, and agitation of 700 rpm. Aliquots were collected at (5 to 25) min. Excess methanol was removed from the resulting product using a rotary vacuum evaporator (Laborota 4000, Heidolph, Germany); the generated glycerin and water were removed by centrifugation (Multifuge X1R-N/S 41464410, ThermoElectron Led GMBH, EUA) at 10,000 rpm for 20 min.

2.5 Determination of fatty acid methyl esters (FAMEs)

The fatty acid ester analysis was performed as described by Bezerra et al. [37]. A gas phase chromatograph coupled to a mass spectrometer (GCMS-QP2010, Shimadzu, Japan) equipped with an autoinjector (AOC-20i, Shimadzu, Japan) and a capillary column Rtx-5MS (30 m × 0.25 mm × 0.25 μm thick film) was used. Helium was employed as the drag gas at a rate of 1.2 mL/min and temperature rate of 4 °C/min, with an injector temperature between 100 °C and 280 °C (5 °C/min), and splitless injection of 1 μL of the supernatant. A quadrupole filter with a scanning rate of (39 to 550) Da/s was used. The electron impact technique was used at 70 eV to achieve ionization. Each substance was identified by comparing its spectral mass to that reported in the literature [38] (Adams, 2017) and the National Institute of Standards and Technology database [39].

2.6 Mathematical modeling

2.6.1 Calculation of kinetic parameters

The experimental data for the highest yield curve obtained at 80 °C and 350 bar were employed for the calculation of the kinetic parameters and mass transfer rates, according to the methodology described by Botelho et al. [36]. The adjustment of a twoline spline was made to estimate the parameters of the first part of the curve, which corresponds to the period of constant extraction rate (CER), i.e., the mass transfer rate in the CER period (M_{CER}), duration of the period (t_{CER}), and mass proportion of solute in the fluid phase at the extractor outlet in the CER period (Y_{CER}), obtained by dividing M_{CER} by the solvent flow rate (8.85×10^{-5} kg/s) during the period of constant extraction.

2.6.2 Modeling of the overall extraction curve (OEC)

The OEC was adjusted with the model by Sovová (2012) [41], which provides several simplified equations able to successfully model the extraction curves of several raw materials. The model is based on the combination of characteristic times for individual periods or phases that can be observed during the extraction process, such as external and internal mass transfer, the time characteristic of mass transfer in the fluid phase (t_{f}), time (t), and mean residence time of the solvent in the extractor (t_{r}) [40,41].

Since a kinetic curve was drawn for oil extraction from PKC using a ground dry sample, it was considered that the extraction with supercritical CO_2 from this type of raw material is very similar to that occurring in the extraction of vegetable oil from seeds described by Sovová [41], where the most applied configuration is a standard plug-flow with no solid matrix interaction. The model considers two periods of extraction in the kinetic curve: the first is dependent on the solute solubility (Y_{sat}) in supercritical CO_2 ($t \leq t_1$), where t_1 is the end of the first extraction period; in the second period, the mass transfer is controlled by diffusion of the vegetable raw material ($t > t_1$).

Mouahid et al. [42] applied the Sovová model [41] using the extraction curve described by the following equations:

At $t \leq t_1$:

$$e = tY_{\mathrm{sat}}\left[1 - exp\left(\frac{-1}{\theta_{\mathrm{f}}}\right)\right]q' \tag{2}$$

where e is the extraction yield, t is the extraction time, θ_f (= t_f/t_r) is the external mass transfer resistance (dimensionless), and q' is the specific flow rate. t_1 and Y_{sat} correspond to the duration of the CER period (t_{CER}) and the mass ratio of the solute in the fluid phase at the extractor outlet in the CER period (Y_{CER}), respectively, both calculated as described in Section 2.6.1.

At $t = t_1$:

$$e_1 = GX_{\mathrm{u}} \tag{3}$$

where G is the initial fraction of extract in the intact cell and X_{u} is the concentration of extract in the solid matrix before extraction.

At $t > t_1$:

$$e = X_{\mathrm{u}}\left[1 - (1 - G)\exp\left(-\frac{t - t_1}{t_{\mathrm{i}}}\right)\right] \tag{4}$$

where t_{i} is the characteristic time of mass transfer of the solid phase (internal diffusion).

G, t_{i}, and θ_{f} are adjustable parameters. As such, parameter θ_{f} was adjusted with eq. (2) from the linear segment of the curve, while G and t_{i} were adjusted with eq. (4) from the second part of the curve. With these parameters, the mass transfer coefficient in the fluid phase (external coefficient) (k_{f}) and the internal mass transfer coefficient (k_{i}) were calculated using the following equation:

$$t_r = \frac{\gamma}{q'} \tag{5}$$

where t_r represents the characteristic time of displacement of the fluid in the extractor (residence time in the plug-flow regime or the mean residence time for an ideal mixer) and γ ($= \rho_f\, \varepsilon/\rho_s(1–\varepsilon)$) is the mass ratio between the solvent and solid in the extractor, where ρ_f is the density of the solvent and ρ_s is the density of the particle.

$$t_f = \frac{\varepsilon}{1-\varepsilon}\frac{\lambda}{k_f},\ \theta_f = \frac{t_f}{t_r} \tag{6}$$

where t_f is the characteristic time of external mass transfer in the fluid phase and ε is the bed porosity.

$$t_i = \frac{\lambda}{k_i} \tag{7}$$

where λ is the characteristic dimension of the particles (volume–surface).

To evaluate the quality of the mathematical fit, the coefficient R^2 and residual sum of squares (RSS) were calculated.

3. Results and Discussion

3.1 Characterization of the raw material

The average particle diameter was 5×10^{-4} m and the true density was (1460 ± 10) kg/m^3. The bed porosity was equal to 0.6986. The values for the moisture content, total protein, ash content, total lipid concentration, and crude fibers are shown in Table 1.

Table 1. Centesimal composition of palm kernel cake before and after extraction with supercritical CO_2

Parameter	Before SFE (%)	After SFE (%)
Moisture	4.11 ± 0.04	4.47 ± 0.14
Ash	7.64 ± 0.050	0.75 ± 0.06
Proteins	12.58 ± 0.121	12.6 ± 0.09
Lipids	7.34 ± 0.228	1.88 ± 0.09
Fibers	35.98 ± 0.453	34.48 ± 0.58
Carbohydrates	32.33 ± 0.617	45.08 ± 0.58

*Mean ± Standard Deviation

The composition of PKC before extraction was compared to that from the works by Ramachandran et al. [43], who described the general composition of various oil cakes including PKC, Sabu et al. [44], Loh et al. [45] and Alimon [46], who employed Malaysian PKC, and Cerveró et al. [14], who studied Indonesian PKC. All residues were obtained by mechanical pressing, as is the case of the present study.

The moisture content (4.11 % ± 0.00 %) was lower than those reported by Ramachandran et al. [43] (10 %), Loh et al. [45] (11%), Sabu et al. [44] (10 %), and Alimon [46] (5.5 % to 12 %). This result reflects the effectiveness of the drying process. For supercritical fluid extraction, the presence of water in the raw material is only acceptable in up to 10 % content as it reduces the contact of the matrix with supercritical CO_2 owing to the pasty consistency of the sample. In these cases, water acts as a barrier to diffusion of the solvent in the sample, as well as to lipid diffusion [47].

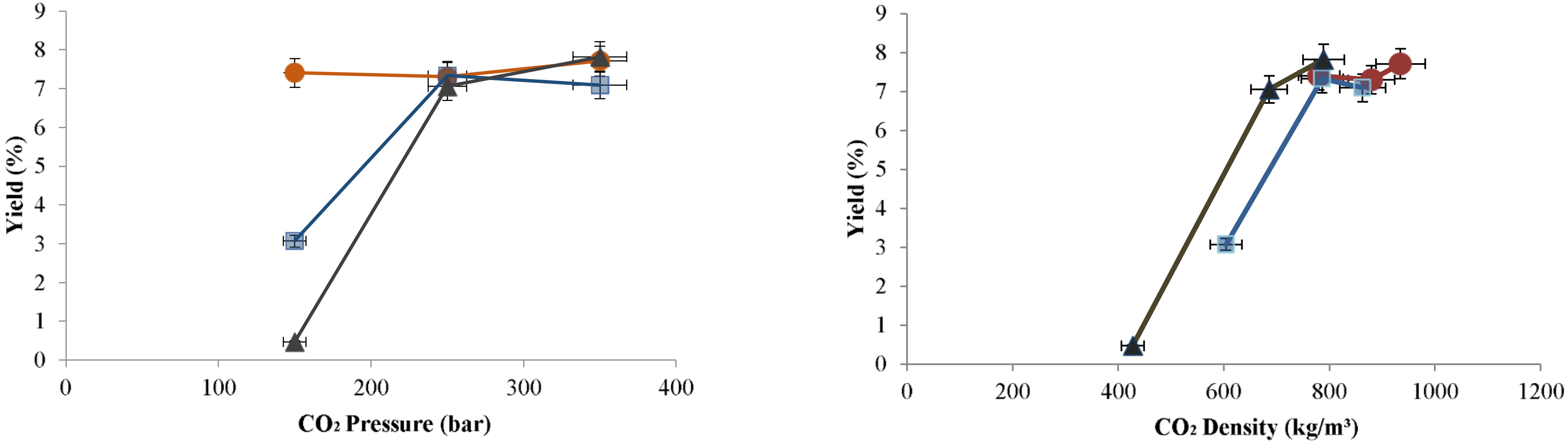
The ash content was 7.64 % ± 0.05 %, the proteins were equal to 12.58 % ± 0.12 %, the fiber content was 35.98 % ± 0.45 %, the lipid concentration of the ether extract had value of 7.34 % ± 0.23 %, and the carbohydrate content of PKC was around 32.33 % ± 0.62 %. Such a high content of lipids is probably due to the not-so-effective industrial extraction process (screw press). The values of proteins and fibers are important since they can be used as feed supplementation for animals. Zahari and Alimon [5] reported that PKC serves as a great source of energy and fiber and that it can be added to cattle feed (30 % to 50 %).

The carbohydrates content also represents an important source for industrial fermentation processes and possible production of biofuels such as bioethanol, as reported by Frederick Jr et al. [48] and Ho et al. [49].

Upon comparing the parameters before and after extraction, no significant changes were observed, except for the lipid value, which was significantly reduced, and the carbohydrate value, which consequently increased. This was expected in view of the report by Hossain et al. [9]. Obviously, the reduction of the lipid content is due to the successful SFE process, which also preserves the nutrients of the raw material.

3.2 SFE global yield isotherms

The global yield for each isotherm relative to the CO_2 pressure and density is shown in Figure 2 (a and b, respectively). The highest yield was obtained at 80 °C and 350 bar (7.82 % ± 0.28 %); however, the fraction obtained at 40 °C and 150 bar was chosen for transesterification experiments. Under this condition, the mass yield was 7.41 % ± 0.45 %. Although this is not the highest yield, factors such as the energy consumption must be taken into account. According to Chemat [51], extraction processes are influenced by environmental and economic factors; hence, such methods should involve the minimum possible energy consumption and waste. Therefore, processes at lower pressures and temperatures must be prioritized.



(a) (b)

Figure 2. Global yield isotherms of palm kernel oil extraction performed with supercritical CO_2 on dry basis versus pressure (a) and versus density (b). (●) 40°C, (■) 60°C, (▲) 80°C.

At 40 °C and 150 bar, the yield obtained was higher than at 60 °C (3.07 % ± 0.64 %) and 80 °C (0.47 % ± 0.13 %) at the same pressure. In this case, the effect of the SFE density prevails. As the temperature increases, at constant pressure, the density decreases, affecting the solute solubility and consequently the yield. Indeed, an increase in temperature raises the vapor pressure of the solute, enhancing its solubility in the supercritical fluid, and therefore, increasing the extraction yield. Actually, the solubility is a function of the supercritical fluid density [12]. Retrograde condensation is observed at approximately 250 bar. The highest yields (7.71 % ± 0.58 % and 7.82 % ± 0.28 %) were obtained for the isotherms at 40 and 80 °C, respectively, both above the inflection point. According to Uquiche et al. [52], at higher pressures ($P \geq 300$ bar), the retrograde condensation conditions disappear since the vapor pressure and volatility of the oil increase. The same behavior has been described by Zaidul et al. [53], who also used carbon dioxide to extract PKO. As in this study, their highest yield was obtained at 40 and 80 °C and pressures above 276 bar. Although their highest yield was 48.9%, much higher than the results in this work, it must be noted that Zaidul et al. [53] used dehulled ground palm kernels while we used PKC.

3.3 Comparison of SFE with Soxhlet extraction

Soxhlet extraction of PKC oil afforded a yield of 7.92 % ± 0.19 %, similar to the highest yield obtained by SFE (7.82 % ± 0.28 %) at 80 °C and 350 bar. Zaidul et al. [53] also compared the oil yields of SFE and Soxhlet methods, confirming their great similarity. However, Soxhlet extraction presents many disadvantages such as the use of toxic and flammable liquid organic solvents (e.g., hexane), hazardous emissions during extraction, non-selective extraction, and very time-consuming operation [54]. Upon comparing the techniques, the best extraction procedure would be the one that does not generate additional pollution, in this case SFE.

Castro et al. [55] reported that the use of supercritical CO_2 for oil extraction offers many important advantages against conventional techniques. The procedures are faster, highly selective, provide high quality extracts, use inexpensive solvents, and can be performed at lower temperatures, and are thus suitable for the extraction of volatile and thermolabile compounds. In this study particularly, a significant yield was achieved at relatively low pressure and temperature, rendering SFE preferable over the Soxhlet method.

Statistical analysis of the SFE conditions and Soxhlet experiments, according to the Tukey test ($p < 0.05$), showed that only the conditions of 60 °C/150 bar and 80 °C/150 bar present statistically different yields in comparison to the other extraction conditions. Therefore, the highest yields obtained in this work, 7.92 % ± 0.19 % (Soxhlet) and 7.82 % ± 0.28 % (SFE), are statistically the same, confirming that supercritical extraction is the most suitable process.

3.4 Fatty acid content in extracts

The fatty acid profiles of the PKO obtained by the supercritical CO_2 and Soxhlet methods are shown in Table 2. Caprylic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) acids were detected for all the SFE operating conditions and in the Soxhlet extracts. The fatty acid with the highest concentration was lauric acid (60.24 % ± 0.62 %), followed by oleic (24.36 % ± 0.71 %), myristic (17.25 % ± 0.29 %), and palmitic (10.31 % ± 0.52 %) acids. The conditions of 150 bar and 60 °C afforded the highest saturated fatty acid content (92.12 %).

Table 2. Composition of fatty acids in palm kernel oils obtained by SFE and Soxhlet techniques (%)

Fatty Acids	40 ºC			60 ºC			80 ºC			
Pressure (bar)	150	250	350	150	250	350	150	250	350	Soxhlet
Density (kg/m^3)	780.2	879.49	934.8	604.1	786.55	862.94	427.15	686.22	788.97	
C8:0	2.66	2.33	2.88	4.34	2.59	2.54	2.76	2.48	2.67	3.01
C10:0	2.79	2.53	2.88	4.37	2.79	2.64	2.69	2.56	2.89	3.06
C12:0	45.55	42.69	45.07	60.24	44.89	42.78	39.43	42.10	45.58	47.85
C14:0	16.43	16.56	15.97	16.37	16.28	15.96	12.70	16.20	16.09	17.25
C16:0	9.53	10.25	9.44	5.66	9.73	10.04	10.08	10.25	9.46	10.31
C18:0	2.40	2.62	2.38	1.14	2.49	2.79	3.35	2.83	2.43	2.63
C18:1	17.77	19.43	18.26	6.97	18.19	20.00	24.36	20.31	17.94	14.43
C18:2	2.88	3.59	3.12	0.90	3.03	3.26	4.63	3.26	2.94	1.19
SFA	79.36	76.98	78.62	92.12	78.77	76.75	71.01	76.42	79.12	84.11
MUFA	17.77	19.43	18.26	6.97	18.19	20.00	24.36	20.31	17.94	14.43
PUFA	2.88	3.59	3.12	0.90	3.03	3.26	4.63	3.26	2.94	1.19

C8:0 (caprylic acid); C10:0 (capric acid); C12:0 (lauric acid); C14:0 (myristic acid); C16:0 (palmitic acid); C18:0 (stearic acid); C18:1 (oleic acid); C18:2 (linoleic acid); SFA (saturated fatty acids); MUFA (monounsaturated fatty acids); PUFA (polyunsaturated fatty acids). The standard deviations for all fatty acids were lower than 1.2%.

When the temperature was increased from 40 to 60 °C, at pressures of 150 and 250 bar, the shorter-chain fatty acid content (C8–C12) increased and the longer-chain fatty acid content (C14–C18:2) decreased. When the temperature was increased from 60 to 80 °C, at both 150 and 250 bar, the shorter-chain fatty acid content decreased (C8–C12) and the longer-chain fatty acid content increased (C14–C18:2). At 350 bar, this behavior reversed in both cases. It can be inferred that the solubility of the C8–C12 and C14–C18:2 fatty acid fractions decreases or increases depending on the operating conditions and on the CO_2 density, since higher densities are achieved at 350 bar. The same trend was reported by Zaidul et al. [53], who compared the fatty acid profile of PKOs obtained by Soxhlet extraction and SFE. In fact, the C8–C18:2 concentrations in their Soxhlet extracts were similar to those found in this study. This was expected because both studies used the same palm species (*Elaeis guineensis*).

3.5 Extraction kinetics and mathematical modeling of the global extraction curve (OEC)

The model proposed by Sovová [41] combines the characteristic times of the individual stages of the extraction process with kinetic curve equations in a simple way, allowing the approximate description of different types of supercritical extraction, such as the extraction of vegetable oil from seeds considering a plug-flow standard system with no solid matrix interaction. For this configuration, two extraction periods are observed: the first depends on the solubility of the solute in supercritical CO_2, while the second is mainly controlled by internal diffusion. The experimental extraction curve and modeling are presented in Figure 3.

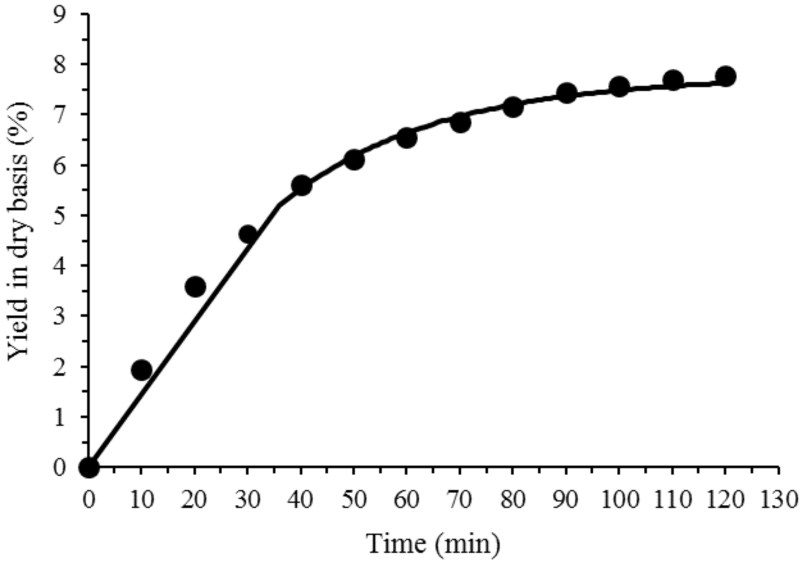


Figure 3. Kinetics of oil extraction from palm kernel cake with supercritical CO_2 obtained at 80ºC and 350 bar and the mathematical modeling. (●) Experimental, (——) Sovová (2012) [41].

Upon comparing the yields of the experimental extraction curves with those calculated, a good adjustment was observed for the two extraction periods (RSS = 1.0705×10^{-4} and $R^2 = 0.9983$), showing that the model is able to satisfactorily describe the curve obtained at 80 °C and 350 bar. The model parameters are given in Table 3.

Table 3. Parameters of Sovová (2012) model [41]

Parameters	80 ºC/350 bar
X_u	0.0777
ρ_s (kg m^{-3})	1460
ρ_{CO_2}(kg m^{-3})	788.97
q' (kg$_{solvent}$ kg$_{solid}^{-1}$ s^{-1})	0.00402
θ_f	0.0287
γ	1,2525
ε	0.6986
λ (m)	0.0005
G	0.67
Y_{sat} (kg$_{solute}$ kg$_{solvent}^{-1}$)	0.006175
t_f (s)	89.43
t_r (s)	311.42

t_i (s)	1752.67
t_1 (s)	2160
k_f (m s^{-1})	1.2958×10^{-5}
k_i = (m s^{-1})	2.8528×10^{-7}
*RSS**	1.0705×10^{-4}
R^2	0.9983

$*RSS=\Sigma(e^{exp} - e^{calc})^2$; *e*: extraction yield (%)

The values of the adjustable parameters *G*, t_i, and θ_f are of the same order as the values provided by Sovová [41], which is satisfactory. The *G* value is closely associated with the degree of fragmentation of the particles; when the oil fraction (*G*) in open cells is <1, the fraction of oil trapped in intact cells (1 – *G*) is extracted much slower than that in open cells. This oil fraction (*G* = 0.67) is extracted at the beginning of the supercritical extraction process, where fast extraction takes place and external mass transfer typically results in a rapid increase of the extraction yield [41,56].

Generally, external mass transfer in the fluid phase is much faster than internal mass transfer in the solid phase. Therefore, the characteristic time for external mass transfer (t_f) should be much lower than the characteristic time for internal mass transfer (t_i) [56]. This was confirmed by the value of the mass transfer coefficient in the fluid phase (k_f = 1.2958×10^{-5} m s^{-1}) being greater than the internal mass transfer coefficient (k_i = 2,093 × 10^{-7} m/s), with t_i = 1752.67 s (29.2 min) being significantly higher than t_f = 89.43 s (1.49 min), which means that mass transfer in the second extraction period is much slower than in the first period, indicating that further yield increases would obviously be more time consuming since slow extraction of the interior of the solid matrix takes place in the second extraction period, which is mainly controlled by internal diffusion.

The low value of t in relation to the residence time value t_r = 311.42 s (5.19 min) indicates that, in the first extraction period, which depends on the solute solubility (Y_{sat}) in supercritical CO_2 ($t \leq t_1$), the supercritical fluid is saturated with extractable solutes and a linear relationship between the yield and extraction time can be expected.

3.6 Characterization of transesterified products

Table 4 shows the ester content obtained at different molar ratios, times, and temperatures. The standard deviations were less than 0.5 % and the ester content ranged from 90.48 % ± 0.10 % to 99.81 % ± 0.10 %. In general, 14 fatty acids esters were identified.

Table 4. Methyl esters identified in the transesterified PKO (%)

MR	T (ºC)	τ (min)	C8:0	C9:0	C10:0	C11:0	C12:0	C13:0	C14:0	C16:0	C18:0	C18:1	C18:2	C20:0	C22:0	C24:0	Total
24:1	250	5	13.02	0.00	6.90	2.15	32.46	0.28	17.82	8.18	4.44	8.14	4.26	0.26	0.00	0.00	97.91^{n}
		10	14.66	0.00	7.54	0.09	26.19	0.11	15.62	9.84	21.09	0.22	0.00	0.39	0.22	0.21	96.18^{j}
		15	13.70	0.00	7.52	0.00	44.15	0.00	13.80	5.57	10.93	0.00	0.00	0.16	0.00	0.06	95.89^{i}
		20	13.30	0.00	7.02	0.00	37.15	0.28	15.26	7.06	15.19	0.00	0.00	0.30	0.00	0.00	95.56^{h}
		25	10.64	0.09	5.87	0.00	37.68	0.08	16.55	7.44	16.84	0.00	0.00	0.17	0.00	0.00	95.36^{g}
	300	5	11.55	0.00	7.24	0.00	34.55	0.00	15.83	9.29	19.77	0.00	0.00	0.29	0.11	0.00	98.63^{p}
		10	10.07	0.00	4.58	0.09	39.36	0.14	17.04	8.82	16.81	0.00	0.00	0.00	0.00	0.00	96.91^{k}
		15	13.02	0.00	6.47	0.17	36.01	0.26	14.59	8.52	15.64	0.00	0.00	0.43	0.17	0.00	95.28^{g}
		20	15.19	0.00	6.32	0.13	39.11	0.04	13.57	6.66	13.51	0.00	0.00	0.36	0.12	0.13	95.14^{f}
		25	16.63	0.00	7.08	0.07	31.54	0.03	12.18	7.06	18.91	0.00	0.00	0.32	0.12	0.13	94.07^{d}
	350	5	14.23	0.00	6.33	0.06	36.69	0.00	13.77	7.71	17.83	0.00	0.00	0.23	0.00	0.00	96.85^{k}

		10	13.83	0.00	7.93	0.05	32.99	0.00	14.43	8.76	18.80	0.00	0.00	0.00	0.00	0.13	96.93^{k}
		15	20.25	0.00	7.06	0.00	32.02	0.00	12.04	8.14	18.27	0.00	0.00	0.00	0.00	0.00	97.78^{m}
		20	16.72	0.00	11.09	0.20	30.56	0.24	13.17	8.06	17.58	0.00	0.00	0.24	0.06	0.00	97.92^{n}
		25	14.06	0.00	4.29	9.06	34.88	0.22	13.32	7.40	15.67	0.00	0.00	0.17	0.00	0.19	99.26^{s}
42:1	250	5	0.00	0.00	0.00	0.00	16.51	0.00	17.53	18.31	47.09	0.00	0.00	0.00	0.00	0.00	99.44^{t}
		10	9.76	0.00	4.93	0.00	32.98	0.00	15.82	7.55	23.81	0.00	0.00	0.00	0.00	0.00	94.85^{e}
		15	9.21	0.08	5.51	0.00	35.36	0.07	15.85	8.07	20.23	0.00	0.00	0.18	0.19	0.06	94.81^{e}
		20	12.82	0.10	5.96	0.00	36.93	0.18	15.75	9.93	18.82	0.00	0.00	0.12	0.00	0.00	90.61^{b}
		25	11.62	0.09	5.87	0.00	37.45	0.08	12.92	6.44	15.84	0.00	0.00	0.17	0.00	0.00	90.48^{a}
	300	5	15.30	0.00	0.00	0.00	36.67	0.12	13.73	8.24	22.95	0.00	0.00	0.20	0.00	0.00	96.21^{j}
		10	12.22	0.12	5.45	0.00	38.34	0.23	11.03	7.27	21.58	0.00	0.96	0.00	0.08	0.00	97.28^{l}
		15	10.63	0.14	4.89	0.00	33.16	0.06	14.16	8.82	26.79	0.00	0.00	0.22	0.10	0.00	98.97^{q}
		20	10.86	0.16	5.03	0.00	33.68	0.18	13.76	8.87	25.30	0.00	1.33	0.21	0.00	0.08	99.10^{r}
		25	11.09	0.14	5.06	0.00	33.00	0.00	13.90	8.74	25.39	0.06	1.49	0.19	0.09	0.00	99.15^{r,s}
	350	5	10.24	0.06	4.97	0.05	39.73	0.00	13.76	8.14	21.97	0.00	0.00	0.22	0.07	0.09	99.81^{u}

		10	6.08	0.00	3.39	0.00	18.95	1.59	7.93	6.57	53.04	0.36	0.00	0.71	0.00	0.00	98.62^{p}
		15	0.10	0.26	2.02	0.00	29.76	0.00	13.21	13.65	39.58	0.00	0.00	0.00	0.00	0.00	98.58^{p}
		20	12.46	0.11	5.96	0.00	35.20	0.00	14.27	8.74	18.81	0.00	2.20	0.29	0.00	0.12	98.16^{o}
		25	12.38	0.00	5.46	0.00	39.55	0.59	14.10	0.16	16.22	0.00	2.13	0.23	0.06	0.09	90.97^{c}

*MR: molar ratio (methanol:oil); T: temperature (°C); τ: time (min). *Different letters indicate significant differences between values ($p < 0.05$) by Tukey test. C8:0 (Octanoic acid); C9:0 (Nonanoic acid); C10:0 (Decanoic acid); C11:0 (Undecanoic acid); C12:0 (Dodecanoic acid); C13:0 (Tridecanoic acid); C14:0 (Tetradecanoic acid); C16:0 (Hexadecanoic acid); C18:0 (Octadecanoic acid); C18:1 (Oleic Acid); C18:2 (Linoleic acid); C20:0 (Eicosanoic acid); C22:0 (Docosanoic acid); C24:0 (Tetracosanoic acid). The standard deviations for all methyl esters were lower than 0.5 %.

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The FAMEs with the highest levels were C8:0 (octanoic acid), C10:0 (decanoic acid), C12:0 (dodecanoic acid), C14:0 (tetradecanoic acid), C16:0 (hexadecanoic acid), and C18:0 (octadecanoic acid). The highest ester content (99.81 % ± 0.10 %) was obtained using a methanol/oil molar ratio of 42:1 at 350 °C in only 5 min. This result is better than that reported by Bunyakiat et al. [57], who investigated the supercritical transesterification of PKO using methanol and obtained a methyl ester conversion of 96% under the same operating conditions (350 °C and methanol/vegetable oil molar ratio of 42:1) with the exception of a longer space time (300 s vs. 400 s). Although the lowest conversion (90.48 % ± 0.10 %) was obtained at 250 °C, molar ratio of 42:1, and 25 min, in any way this value can be considered a bad result. On the other hand, the longer the reaction is, the more expensive the process becomes. Thus, shorter processes are preferable.

With respect to the thermal stability of the fatty acids present in the PKO in the transesterification process, Moulodi et al. [64] states that the presence of oleic acid (unsaturated fatty acid) in olive oil, also found in PKO oil fractions, increases the thermal stability of the product during heating process. Also, Queiroga Neto et al. (2009) [65] reported that some substances present in the oil such as carotenoids, sterols, phenolic compounds, tocopherols, and others have been considered as responsible for thermal stability. In fact, α-tocopherol, sterol and α-tocotrienol were found in PKO obtained from PKC by SFE in the work of Krishnaiah et al. (2012) [66]. Therefore, such substances may be responsible for the thermal stability of PKO.

According to Musa [58], the reaction parameters generally investigated in supercritical transesterification reactions are the temperature, pressure, alcohol/oil molar ratio, and reaction time. In this study, 200 bar was kept constant for all experiments. Silva and Oliveira [29] stated that the maximum pressure that can be used in batch transesterification reactions is 200 bar, because operating pressures above this value might not be industrially viable, e.g., higher pressures mean increased costs.

According to Ngamprasertsith and Sawangkeaw [59], the temperature is the most important parameter influencing the supercritical transesterification reaction, since it accelerates the chemical kinetics and changes the alcohol properties. Demirbas [26] stated that increasing the reaction temperature has a positive influence on the conversion of esters. This parameter, combined with a certain molar ratio, provides a high FAME conversion. Since methanol is the reacting alcohol, a high molar ratio shifts the reaction equilibrium toward the products, resulting in higher solubility of the alcohol in the oil and thus increased methyl ester conversion [60]. Such behavior was observed in this study: the highest FAME conversion was obtained at the highest temperature and methanol/oil molar ratio.

Regarding the effect of the reaction time on the FAME conversion, it can be seen in Figure 4 that only 5 min of reaction was sufficient to produce over 96 % of methyl esters under all the conditions studied. Saka et al. [61] and Yin et al. [62] also reported high FAME conversions from vegetable oils in short times using supercritical methanol.

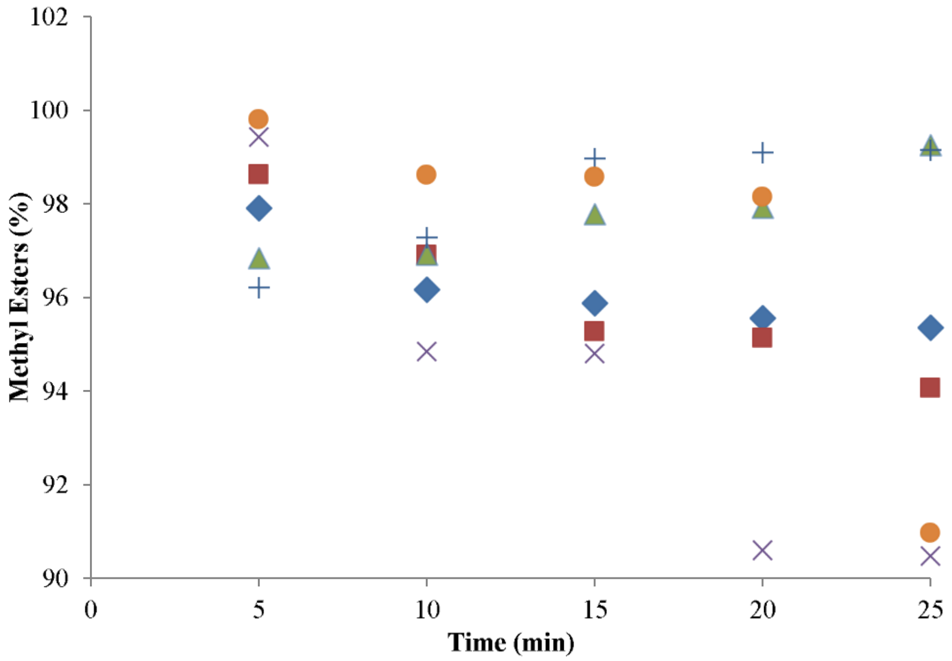

Figure 4. Effect of reaction time on the yield of fatty acids methyl esters (◆) 24:1 250°C, (■) 24:1 300°C, (▲) 24:1 350°C, (×) 42:1 250°C, (+) 42:1 300°C, (●) 42:1 350°C

4. Conclusions

Transesterification of PKO from PKC by a non-catalytic supercritical method was successfully performed. A conversion of 99.81 % ± 0.10 % of fatty acid methyl esters was achieved in only 5 min at a methanol/oil molar ratio of 42:1 and 350 °C. This process shows great advantages over conventional techniques that justify its implementation; however, studies on the technical and economical limitations of the method are still required.

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kernel cake.

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CAPÍTULO 6

1. CONCLUSÃO GERAL

A transesterificação do óleo residual da torta de palmiste pelo método supercrítico não-catalítico também foi realizada com sucesso. 99,81% de ésteres metílicos de ácidos graxos, correspondendo a um rendimento de 93,55%, foram alcançados em apenas 5 min, usando relação molar de 1:42 (óleo:metanol) e temperatura de 350 °C. Este processo mostra fortes vantagens sobre a técnica convencional que justifica sua implementação; no entanto, estudos considerando as limitações técnicas e econômicas do método devem ser realizados.

CAPÍTULO 7

APÊNDICE: PRODUÇÃO ACADÊMICA DURANTE O PERÍODO DO DOUTORADO

7.1 Trabalhos completos publicados em anais de congressos

1. COSTA, W. A.; LIMA, C. R. ; SILVA FILHO, F. G. S. ; SILVA, C. C. E. ; MARTELLI, M. C. ; BRASIL, D. S. B. . SIMULATION OF BENZENE ADSORPTION ONTO ACTIVATED CARBON. In: XXII CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA, 2018, São Paulo.

2. COSTA, W. A.; OLIVEIRA, M. S. ; SILVA, A. P. S. E. ; SILVA FILHO, F. G. S. ; Bezerra, Fernanda Wariss Figueiredo ; MARTELLI, M. C. . DEVELOPMENT OF CERAMICS ENAMEL USING BOTTLE GLASS. In: XXII CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA, 2018, São Paulo.

3. PINTO, RAFAEL H. H. ; FERREIRA, M. C. R. ; COSTA, W. A. ; CORDEIRO, RENATO MACEDO ; DE AGUIAR ANDRADE, ELOISA HELENA ; CARVALHO JUNIOR, R. N. . CHEMICAL CHARACTERIZATION OF PERPÉTUA-ROXA (Centratherum punctatum Cass.) ESSENTIAL OIL EXTRACTED BY HYDRODISTILLATION. In: XXII CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA, 2018, São Paulo.

4. CORDEIRO, RENATO MACEDO ; BEZERRA, F. W. F. ; PINTO, RAFAEL H. H. ; COSTA, W. A. ; OLIVEIRA, M. S. ; CARVALHO JUNIOR, R. N. . DETERMINAÇÃO DE CAROTENOIDES EM EXTRATOS DE MURICI (BYRSONIMA CRASSIFOLIA L. RICH) OBTIDOS POR EXTRAÇÃO COM FLUIDO SUPERCRÍTICO. In: XXII CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA, 2018, São Paulo.

5. BEZERRA, F. W. F.; BEZERRA, P. N. ; OLIVEIRA, M. S. ; **COSTA, W. A.;** CARVALHO JUNIOR, R. N. ; DE AGUIAR ANDRADE, ELOISA HELENA . IDENTIFICAÇÃO E QUANTIFICAÇÃO QUÍMICA DO ÓLEO ESSENCIAL DE PIPER ADUNCUM L.. In: XXVI CONGRESSO BRASILEIRO DE CIÊNCIA E TECNOLOGIA DE ALIMENTOS, 2018, Belém.

6. TUMA, J. C. ; PINTO, R. H. H. ; CORDEIRO, R. M. ; **COSTA, W. A**. ; SILVA, A. P. S. E. ; CARVALHO JUNIOR, R. N. . CINÉTICA DE SECAGEM DA POLPA DE AÇAÍ (EUTERPE OLERACEA, MART.). In: XXVI CONGRESSO BRASILEIRO DE CIÊNCIA E TECNOLOGIA DE ALIMENTOS, 2018, Belém.

7. **COSTA, W. A**.; OLIVEIRA, M. S. ; BEZERRA, F. W. F. ; BEZERRA, P. N. ; CARVALHO JUNIOR, R. N. ; SOUZA FILHO, A. P. S. . PHYSICO-CHEMICAL AND NUTRITIONAL CHARACTERIZATION OF COWPEA BEANS (VIGNA UNGUICULATA L. WALP.) FERTILIZED WITH K2O. In: XXVI CONGRESSO BRASILEIRO DE CIÊNCIA E TECNOLOGIA DE ALIMENTOS, 2018, Belém.

8. MENEZES, E. G. O. ; **COSTA, W. A.** ; BEZERRA, F. W. F. ; OLIVEIRA, M. S. ; BEZERRA, P. N. ; CARVALHO JUNIOR, R. N. . PREDIÇÃO DAS PROPRIEDADES FÍSICAS E TERMODINÂMICAS DO ÓLEO DE PALMISTE POR METODOLOGIA DE

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9. COSTA, W. A.; SILVA, C. J. ; LIMA, C. R. ; OLIVEIRA, M. S. ; GARCIA, K. C. S. P. ; SANTOS, A. P. M. ; SILVA, A. P. S. E. ; CARVALHO JUNIOR, R. N. ; MARTELLI, M. C. ; BRASIL, D. S. B. . PROPRIEDADES FÍSICAS DA ADSORÇÃO DE BTX SOBRE CARVÃO ATIVADO. In: 15º Encontro de Profissionais da Química da Amazônia, 2017, Belém.

10. **COSTA, W. A.**; OLIVEIRA, M. S. ; PINTO, R. H. H. ; GARCIA, K. C. S. P. ; SANTOS, A. P. M. ; SILVA, C. J. ; BEZERRA, F. W. F. ; CARVALHO JUNIOR, R. N. ; SOUZA FILHO, A. P. S. . CARACTERIZAÇÃO FÍSICO-QUÍMICA E NUTRICIONAL DE FEIJÃO-DA-COLÔNIA (Vigna unguiculata L. Walp.) ADUBADO COM P2O5. In: 15º Encontro de Profissionais da Química da Amazônia, 2017, Belém.

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13. OLIVEIRA, M. S. ; OLIVEIRA, H. A. ; MENEZES, C. ; PEREIRA, D. S. ; CORDEIRO, H. K. C. ; **COSTA, W. A.** ; VASCONCELOS, M. A. M. ; VENTURIERI, G. C. ; SOUZA FILHO, A. P. S. . ANÁLISE QUALITATIVA DE COMPOSTOS FENÓLICOS E ÍNDICE DE OXIDAÇÃO EM AMOSTRAS DE GEOPRÓPOLIS E PRÓPOLIS DE ABELHAS SEM FERRÃO DO ESTADO DO PARÁ. In: 56° CONGRESSO BRASILEIRO DE QUÍMICA, 2016, Belém.

14. COSTA, W. A.; BEZERRA, F. W. F. ; SANTOS, A. P. M. ; CORDEIRO, R. M. ; TUMA, J. C. ; PINTO, R. H. H. ; OLIVEIRA, M. S. ; CARVALHO JUNIOR, R. N. . CARACTERIZAÇÃO FÍSICO-QUÍMICA DA TORTA RESULTANTE DO PROCESSAMENTO DA AMÊNDOA DO DENDÊ (Elaeis guineensis Jacq.). In: 56° CONGRESSO BRASILEIRO DE QUÍMICA, 2016, Belém.

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7.2 Resumos expandidos publicados em anais de congressos

1. CORDEIRO, R. M. ; OLIVEIRA, M. S. ; CUNHA, V. M. B. ; PINTO, R. H. H. ; SILVA, N. J. N. ; **COSTA, W. A.** ; BEZERRA, V. M. S. ; BOTELHO, J. R. S. ; CARVALHO JUNIOR, R. N. . DETERMINAÇÃO DE CAROTENOIDES TOTAIS EM ÓLEOS DE MURUCI (Byrsonima crassifólia L. Rich) OBTIDOS POR DIFERENTES MÉTODOS DE EXTRAÇÃO: CO2 SUPERCRÍTICO E SOLVENTE ORGÂNICO LÍQUIDO. In: XIX Encontro Nacional e V Congresso Latino Americano de Analistas de Alimentos, 2015, Natal - RS. Anais do XIX Encontro Nacional e V Congresso Latino Americano de Analistas de Alimentos, 2015, Natal.

7.3 Trabalhos completos aceitos em eventos em 2018

1. COMPOSIÇÃO DE ÁCIDOS GRAXOS DE ÓLEO DE PALMISTE OBTIDO POR EXTRAÇÃO SUPERCRÍTICA. *In:* 58º Congresso Brasileiro de Química, 2018, São Luís.

2. ANÁLISE DAS INTERAÇÕES ENTRE NITROSAMINAS E CYP2A13 USANDO ANCORAGEM MOLECULAR E SIMULAÇÕES DE DINÂMICA MOLECULAR. *In:* 58º Congresso Brasileiro de Química, 2018, São Luís.

3. TRANSESTERIFICAÇÃO SUPERCRÍTICA DE ÓLEO DE PALMISTE USANDO METANOL. *In:* 58º Congresso Brasileiro de Química, 2018, São Luís.

4. TEOR DE COMPOSTOS FENÓLICOS TOTAIS E FLAVONOIDES TOTAIS EM GEOPRÓPOLIS E PRÓPOLIS DE ABELHAS SEM FERRÃO DA AMAZÔNIA ORIENTAL. *In:* 58º Congresso Brasileiro de Química, 2018, São Luís.

5. EFEITO FITOTÓXICO DO ÓLEO ESSENCIAL DE *Lippia Thymoides* Mart. & Schauer (Verbenaceae). *In:* 58º Congresso Brasileiro de Química, 2018, São Luís.

6. CINÉTICA DE EXTRAÇÃO DO ÓLEO DA POLPA DE AÇAÍ (*Euterpe Oleraceae*) COM CO2 SUPERCRÍTICO: EXPERIMENTOS E MODELAGEM MATEMÁTICA. *In:* 58º Congresso Brasileiro de Química, 2018, São Luís.

7.4 Artigos publicados em periódicos

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2. JCR Bezerra, Fernanda Wariss Figueiredo ; **DA COSTA, WANESSA ALMEIDA** ; de Oliveira, Mozaniel Santana ; DE AGUIAR ANDRADE, ELOISA HELENA ; DE CARVALHO, RAUL NUNES . Transesterification of Palm Pressed-Fibers (Elaeis guineensis Jacq.) Oil by Supercritical Fluid Carbon Dioxide with Entrainer Ethanol. JOURNAL OF SUPERCRITICAL FLUIDS JCR, v. 136, p. 136-143, 2018.

3. JCR CORDEIRO, R. M. ; SILVA, A. P. S. E. ; PINTO, R. H. H. ; **COSTA, W. A.** ; SILVA, S. H. M. ; PINHEIRO, W. B. S. ; DE CARVALHO, RAUL NUNES . Supercritical CO2 extraction of ucuúba (Virola surinamensis) seed oil: global yield, kinetic data, fatty acid profile, and antimicrobial activities. CHEMICAL ENGINEERING COMMUNICATIONS JCR, v. 205, p. 1-12, 2018.

4. MOZANIEL, SANTANA DE OLIVEIRA ; **WANESSA ALMEIDA DA COSTA** ; FERNANDA, WARISS FIGUEIREDO BEZERRA ; MARILENA, EMMI ARAÚJO ; GRACIALDA, COSTA FERREIRA ; RAUL, NUNES DE CARVALHO JUNIOR . Phytochemical profile and biological activities of Momordica charantia L. (Cucurbitaceae): A review. AFRICAN JOURNAL OF BIOTECHNOLOGY, v. 17, p. 829-846, 2018.

5. CRUZ, J. N. ; OLIVEIRA, M. S. ; VOGADO, J. H. ; SILVA, S. G. ; **COSTA, W. A.** ; BEZERRA, F. W. F. ; COSTA, R. A. ; CARVALHO JUNIOR, R. N. ; C. NETO, A. M. J. . Molecular Insights on the Interactions of Nitrosamines from Cigarette Smoking with CYP2A13 using Molecular Docking and Molecular Dynamics Simulation. Journal of Pulmonary Medicine and Respiratory Research, v. 4, p. 1-6, 2018.

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7. JCR de Oliveira, Mozaniel Santana ; **DA COSTA, WANESSA ALMEIDA** ; PEREIRA, DANIEL SANTIAGO ; BOTELHO, JOSÉ RAFAEL SANTOS ; DE ALENCAR MENEZES, TATIANY OLIVEIRA ; DE AGUIAR ANDRADE, ELOISA HELENA ; DA SILVA, SILVIA HELENA MARQUES ; DA SILVA SOUSA FILHO, ANTONIO PEDRO ; DE CARVALHO, RAUL NUNES . Chemical composition and phytotoxic activity of clove (Syzygium aromaticum) essential oil obtained with supercritical CO2. JOURNAL OF SUPERCRITICAL FLUIDS JCR, v. 118, p. 185-193, 2016.

7.5 Capítulos de livro publicados

1. Oliveira, Mozaniel Santana de ; Costa, Wanessa Almeida Da ; Bezerra, Priscila Nascimento ; Filho, Antonio Pedro da Silva Souza ; Junior, Raul Nunes de Carvalho . Potentially Phytotoxic of Chemical Compounds Present in Essential Oil for Invasive Plants Control: A Mini-Review. Biological Approaches for Controlling Weeds. 1ed.: InTech, 2018, v. , p. 1-61.

2. CUNHA, VÂNIA MARIA BORGES; SILVA, MARCILENE PAIVA DA ; **COSTA, WANESSA ALMEIDA DA** ; OLIVEIRA, MOZANIEL SANTANA DE ; BEZERRA, FERNANDA WARISS FIGUEIREDO ; MELO, ANSELMO CASTRO DE ; PINTO, RAFAEL HENRIQUE HOLANDA ; MACHADO, NELIO TEIXEIRA ; ARAUJO, MARILENA EMMI ; JUNIOR, RAUL NUNES DE CARVALHO . Carbon dioxide use in high-pressure extraction processes. Carbon dioxide chemistry, capture and oil recovery. 1ED.: INTECH, 2018, V., p. 211-238.

3. OLIVEIRA, M. S.; **COSTA, W. A.**; BEZERRA, F. W. F.; CARVALHO JUNIOR, R. N. COMPOSIÇÃO QUÍMICA E ATIVIDADES BIOLOGICAS DE ESPÉCIE DA FAMILÍA POACEAE. POACEAE Barnhart. 1ed.Belém: Marques Editora, 2017, v. 1, p. 199-219.

4. JCR **DA COSTA, WANESSA ALMEIDA**; de Oliveira, Mozaniel Santana ; da Silva, Marcilene Paiva ; Cunha, Vania Maria Borges ; Pinto, Rafael Henrique Holanda ; Bezerra, Fernanda Wariss Figueiredo ; Junior, Raul Nunes de Carvalho . Açaí (Euterpe oleracea) and Bacaba (Oenocarpus bacaba) as Functional Food. Superfood and Functional Food - An Overview of Their Processing and Utilization. 1ed.: InTech, 2017, v. , p. 155-172.

7.6 Artigos aceitos para publicação

1. DA COSTA, WANESSA ALMEIDA; BEZERRA, F. W.; de Oliveira, M. S.; DE ANDRADE, E. H. A.; DOS SANTOS, A. P. M.; CUNHA, V.M. B; DOS SANTOS, D. C. S.; BANNA, D. A. D.; DE CARVALHO JUNIOR, R. N. Supercritical CO2 Extraction and Transesterification of the Residual Oil from Industrial Palm Kernel Cake with Supercritical Methanol. JOURNAL OF SUPERCRITICAL FLUIDS, 2018.

2. MEDEIROS, I. G. ; CRUZ, J. N. ; OLIVEIRA, M. S. ; COSTA, W. A. ; LIMA, L. H. A. ; BRASIL, L. S. N. S. ; CARVALHO JUNIOR, R. N. ; C. NETO, A. M. J. ; BRASIL, D. S. B. . Removal of Organic Pollutants Benzene and Phenol Using Nanofiltration: A Molecular Dynamics Study. JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY, 2018.

3. DA COSTA, R.A.; SILVA, S. G.; CRUZ, J. N.; DA COSTA, W.A.; DOS SANTOS, S.; SILVA, R.; SANTOS, C.; ALVES, C.N.; BRASIL, D.S.B. Theoretical study via DFT for prediction of 13C and 1H NMR data of two diterpenoids derived from the root of salvia grandifolia. Journal of the Serbian Chemical Society, 2018.

7.7 Artigos submetidos

1. Planting and seasonal and circadian evaluation of a thymol-type oil from *Lippia thymoides* Mart. & Schauer
2. Bioactive compounds and biological activity of Croton species (*Euphorbiaceae*): an overview.
3. Cytotoxic, antimicrobial activity of the *Syzygium aromaticum* essential oil, molecular docking and dynamics molecular studies of its major chemical constituent.
4. *Piper divaricatum* G.Mey (*Piperaceae*). Essential Oil a Potential Inhibitor of Acetylcholinesterase, Molecular Docking and Molecular Dynamics Simulation of Interaction