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RAMON SOUSA BARROS FERREIRA

PRODUÇÃO DE BIODIESEL A PARTIR DA OLEÍNA DE PALMA UTILIZANDO RESINA ANIÔNICA FORTEMENTE BÁSICA COMO CATALISADOR HETEROGÊNEO

BIODIESEL PRODUCTION FROM PALM OLEIN USING STRONGLY BASIC ANIONIC RESIN AS HETEROGENEOUS CATALYST

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Dissertação apresentada à Faculdade de Engenharia de Alimentos da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Mestre em Engenharia de Alimentos.

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RESUMO

Biodiesel é um biocombustível comumente obtido a partir da reação de transesterificação entre uma molécula de triacilglicerol com três moléculas de um álcool de cadeia curta, na presença de um catalisador homogêneo ou heterogêneo. Estudos envolvendo o uso de catalisadores heterogêneos têm se destacado devido à vantagem de poderem ser facilmente separados para sua reutilização e, dessa forma, reduzir as etapas de purificação do produto. Levando isto em consideração, este trabalho teve por objetivo estudar a conversão em biodiesel etílico a partir da oleína de palma utilizando a resina aniônica Purolite A503S como catalisador heterogêneo. Inicialmente, foram feitas a determinação e a avaliação das características físicas e químicas da oleína de palma. Com o auxílio de um planejamento experimental com delineamento composto central rotacional (DCCR) com dois níveis e três fatores, seis pontos axiais e três repetições no ponto central, foram avaliados os efeitos e as interações dos efeitos da temperatura (33,1 °C, 38,5 °C, 46,5 °C, 54,5 °C, e 60 °C), da porcentagem de catalisador em relação a massa de oleína de palma (10,8 %, 12,5,0 %, 15,0 %, 17,5 % e 19,2 %) e da razão molar oleína de palma:etanol (1:7,96, 1:10, 1:13, 1:16 e 1: 18,04) sobre a porcentagem de conversão em ésteres etílicos. O tempo de reação de 10 horas foi estabelecido através de uma cinética de reação longa e a velocidade de agitação foi determinada avaliando o potencial de conversão e a morfologia da resina, analisada por MEV, variando de 250 a 1000 rpm. As reações foram realizadas em um reator encamisado, acoplado a um banho termostático. Para o cálculo da conversão em biodiesel, os produtos da reação foram quantificados em triacilglicerois, diacilglicerois, monoacilglicerois, ésteres etílicos e etanol pelo método HPSEC e glicerol por estequiometria. Como acima de 400 rpm não houve aumento significativo na conversão e nenhum efeito da agitação foi observado sobre a morfologia da resina, este valor foi mantido constante. A partir dos 17 ensaios do planejamento fatorial, um modelo de segunda ordem foi ajustado aos dados experimentais e, pela análise estatística, foi considerado preditivo e significativo para explica-los. A partir das variáveis otimizadas (17,5 % de catalisador, razão molar óleo:etanol de 1:13 e temperatura de 50,1 °C) foi obtida uma conversão de 98% em ésteres etílicos. Dessa forma, nas condições estudadas, apesar do longo tempo de reação, a resina Purolite A503S se apresenta como um catalisador heterogêneo em potencial para uso em reações de transesterificação e a agitação não apresentou nenhum efeito sobre as características morfológicas da resina.

ABSTRACT

Biodiesel is a biofuel commonly obtained from the transesterification reaction between a molecule of triacylglycerol with three molecules of a short chain alcohol in the presence of a homogeneous or heterogeneous catalyst. Studies involving the use of heterogeneous catalysts have been highlighted due to the advantage that this can be easily separated for their reuse and, thus, reduce product purification steps. Taking into account, this research aimed to study the conversion of palm olein in ethylic biodiesel using the anionic resin Purolite A503S as a heterogeneous catalyst. Initially, the physical and chemical characteristics of palm olein were determined and evaluated. With the help of a central composite rotatable design (CCRD) with two-level, three-factor, six axial points and three repetitions at the central point, the effects and interactions of the effects of temperature (33.1 °C, 38.5 °C, 46.5 °C, 54.5 °C, and 60 °C), of the percentage of catalyst relative to palm olein mass (10.8%, 12.5%, 15.0 %, 17.5% and 19.2%) and of the palm olein:ethanol molar ratio (1:7.96, 1:10, 1:13, 1:16 and 1:18.04) were evaluated on the percentage of conversion to ethyl esters. The reaction time of 10 hours was established by long reaction kinetics, the stirring speed was determined by assessing the conversion potential and the resin morphology was analyzed by SEM, ranging from 250 to 1000 rpm. Reactions were performed in a jacketed reactor coupled to a thermostatic bath. For the calculation of conversion to biodiesel, the reaction products were quantified in triacylglycerols, diacylglycerols, monoacylglycerols, ethyl esters and ethanol by the HPSEC method and glycerol by stoichiometry. As there was no significant increase in conversion for agitation speeds above 400 rpm, no effect of agitation was observed on resin morphology, and this value was kept constant. From the 17 factorial design trials, a second order model was adjusted to the experimental data and, by statistical analysis, was considered predictive and significant to explain them. From the optimized variables (17.5 % catalyst, oil:ethanol molar ratio 1:13 and temperature 50.1 °C), a conversion of 98.0 % in ethyl esters was obtained. Thus, under the studied conditions, despite the long reaction time, Purolite A503S resin presents itself as a potential heterogeneous catalyst for use in transesterification reactions and, the agitation showed no effect on resin morphological characteristics.

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-INTRODUÇÃO E OBJETIVOS GERAL E ESPECÍFICOS-

1 INTRODUÇÃO

Já é bastante evidente que o combate às alterações climáticas necessita de mudanças urgentes na forma como a energia é produzida e a substituição de recursos energéticos fósseis por energias renováveis se faz bastante necessária (BENTSEN; MØLLER, 2017). O biodiesel aparece no cenário bioenergético como uma fonte de substituição aos combustíveis fósseis e se tornou um tema de pesquisa muito relevante devido a sua ampla utilização no setor energético e de transporte (BOLOY et al., 2017). Nos últimos 10 anos mais de 28 mil estudos relacionados à produção e consumo de biodiesel foram publicados em plataformas de pesquisa online, confirmando o que foi dito por Boloy et al. (2017).

Segundo projeções da Agência Internacional de Energia, a produção de biocombustíveis aumentará de 1,3 milhões de barris/dia de 2012 para 4,6 milhões de barris de biodiesel por dia até 2040 e sua participação será de 8 % na demanda de combustíveis para transportes rodoviários (SINGH et al., 2015).Portanto, devido a exigência renovável, o biodiesel provavelmente irá desempenhar um papel importante no crescimento da demanda de combustíveis nas próximas décadas (HOSSEINZADEH-BANDBAFHA et al., 2018).

Convencionalmente, o biodiesel é o produto obtido via transesterificação de óleos vegetais ou gordura animal. Na reação, uma molécula de triacilglicerol (encontrada em maior quantidade em óleos vegetais) reage com um álcool de cadeia curta, mais comumente o metanol ou etanol, na presença de um catalisador, produzindo assim, ésteres metílicos ou etílicos e glicerol (FELIZARDO et al., 2006).

A oleína de palma é um produto obtido através da operação de fracionamento em modo descontínuo ou batelada do óleo de palma refinado e apresenta em seu perfil de ácidos graxos aproximadamente 36,00 % de ácido palmítico (C16:0), 46,60 % de ácido oleico (C18:1) e 10,20 % de ácido linoleico (C18:2), implicando em um óleo com quantidades majoritárias em ácidos graxos insaturados de cadeia longa apresentando aspecto líquido a temperatura ambiente (25 °C) (ALVA, 2016). Essas características podem representar uma grande vantagem para utilização na produção de biodiesel; por exemplo, matérias-primas com menores quantidades de ácidos graxos saturados produzem ésteres etílicos ou metílicos com menor ponto de turbidez. Ou seja, são propícias para utilização em regiões que experimentam temperaturas mais baixas; como por exemplo, no sul do Brasil. Pois, matérias-primas com quantidades altas de ácidos graxos saturados podem causar entupimento em motores de veículos devido à formação de cristais (CARDOSO et al., 2014).

Diferentes tipos de catalisadores podem ser utilizados para acelerar a reação de transesterificação, podendo ser classificados principalmente em catalisadores homogêneos e heterogêneos.

Os catalisadores homogêneos usados para as reações de alcoólise podem ser de natureza ácida ou básica. Industrialmente, catalisadores básicos são mais comumente aplicados para produção de biodiesel (AVHAD; MARCHETTI, 2016). Porém, o seu uso apresenta muitas desvantagens, como a necessidade de se usar uma grande quantidade de água na purificação do biodiesel e não podem ser reutilizados ou regenerados, pois sua separação é difícil e requer equipamentos especializados que podem resultar num aumento dos custos de produção (EVANGELISTA et al., 2016; FREEDMAN; PRYDE; MOUNTS, 1984).

Os catalisadores heterogêneos têm surgido como uma alternativa viável para substituição dos catalisadores homogêneos, objetivando superar as desvantagens citadas acima (ZABETI et al., 2009).

Os catalisadores heterogêneos não são dissolvidos na mistura, podendo ser separados dos produtos facilmente. Como vantagem, os produtos não contêm impurezas do catalisador e os custos de separação são reduzidos (EVANGELISTA et al., 2016). Esses catalisadores possuem também duas vantagens benéficas para a indústria e o meio ambiente, pois podem ser facilmente regenerados e reutilizados. Durante a reação não há a formação de sabão no processo o que simplifica os processos de lavagem, separação e purificação após a reação. Dessa forma, podem ser considerados ecologicamente corretos, uma vez que necessitam de menores quantidades de água para purificação do produto desejado (DOSSIN et al., 2006; EVANGELISTA et al., 2016).

Como forma de superar os problemas causados por catalisadores homogêneos, diversos catalisadores sólidos heterogêneos têm sido estudados na literatura. No entanto, nenhum estudo envolvendo a utilização da resina troca aniônica fortemente básica Purolite A503S como catalisador heterogêneo, foi encontrado na literatura, justificando o seu uso. Com isso, este trabalho teve por objetivo estudar a conversão de biodiesel a partir da oleína de palma utilizando a resina aniônica Purolite A503S como catalisador heterogêneo e etanol como solvente.

2 OBJETIVOS

2.1 Objetivo Geral

O objetivo geral deste trabalho foi investigar a produção de ésteres etílicos a partir da oleína de palma utilizando como catalisador heterogêneo a resina aniônica Purolite A503S.

2.2 Objetivos específicos

Inicialmente foi feita a determinação e avaliação das características físicas e químicas da oleína de palma, em seguida, foi desenvolvido os seguintes objetivos específicos:

- Foi investigado o tempo de reação e a velocidade de agitação na porcentagem de conversão com o uso da resina aniônica;
- Através do planejamento experimental de delineamento composto central rotacional (DCCR) foram determinados os efeitos das variáveis independentes: razão molar etanol: oleína de palma, porcentagem de catalisador e temperatura na conversão da oleína de palma em biodiesel para o tempo e agitação pré-defenidos;
- Otimizar as variáveis independentes pela máxima conversão e validar experimentalmente esse ponto de ótimo;

3 ORGANIZAÇÃO DOS CAPÍTULOS

Este trabalho está dividido em 4 capítulos, onde no **Capítulo 1** uma breve introdução e os objetivos geral e específicos foram apresentados. No **Capítulo 2** foi feita uma revisão na literatura sobre a produção e características do óleo e oleína de palma. Além disso, foi apresentado também o mecanismo da reação de transesterificação e explanado a utilização dos álcoois mais utilizados nas reações para produção de biodiesel. Uma explicação sobre os métodos catalíticos, como catálise homogênea, heterogênea e enzimática assim como uma revisão referente a utilização de resinas de troca iônica para produção de ésteres alquílicos, condições reacionais e mecanismos de reação também foram mostrados.

No **Capítulo 3**, está contido o artigo de revisão publicado na revista Food and Public Health. Neste artigo, foram mostrados os recentes trabalhos publicados na literatura envolvendo a utilização de diferentes catalisadores heterogêneos para produção de biodiesel. Os mecanismos de reação assim como modelos e parâmetros cinéticos também foram abordados neste capítulo

No **Capítulo 4** encontra-se o artigo que será submetido na revista Renewable Energy, neste trabalho contém todas as metodologias utilizadas para o desenvolvimento do trabalho, assim como, os resultados obtidos. Por fim, no **Capítulo 5** uma discussão e conclusão geral a respeito de todo o trabalho são apresentadas.

CAPÍTULO 2

-REVISÃO BIBLIOGRÁFICA-

2 REVISÃO BIBLIOGRÁFICA

2.1 Óleo de palma

O óleo de palma é o principal óleo vegetal produzido hoje no mundo. E apresenta em sua composição cerca de 87 a 92 % de triacilgliceróis, de 3 a 8 % de diacilgliceróis, de 0 a 0,5 % de monoacilgliceróis, 1 a 5 % de ácidos graxos livres e aproximadamente 1 % de componentes menores que incluem: carotenóides, tocoferóis, esteróis, glicolipídeos, fosfolipídios, álcoois triterpênicos e hidrocarbonetos.(Trujillo-Quijano, 1997)

Com apenas 10 % da área plantada de soja, a palma (*Elaeis guineenses*) possui a mesma capacidade de produção em termos de óleo bruto. Só isso já explica o grande interesse em sua produção, visto que, reduz bastante o desmatamento para o plantio de matérias-primas oleaginosas. A palma além de apresentar uma alta produtividade se destaca também por apresentar um baixo custo de produção, tornando-se uma excelente matéria-prima para produção de alimentos e geração de energia (CORLEY, 2009). Quando comparada com outras culturas oleaginosas, como a canola, o girassol ou a soja, o óleo de palma tem o menor uso de combustível, fertilizantes e pesticidas por tonelada produzida (LEVERMANN; SOUZA, 2014).

A Malásia e a Indonésia têm sido o centro de produção do óleo de palma e juntas respondem por cerca de 85 % da produção mundial (USDA, 2019). O Brasil no ranking de produtores mundiais ocupa a 10ª. posição, como mostra a Tabela 1. Em 2016, a produção de óleo de palma no Brasil atingiu cerca de 346 mil toneladas, e outras 192 mil toneladas foram importadas. Para 2018, foi estimado pela Associação Brasileira de Produtores de Óleo de Palma (ABRAPALMA) que a produção nacional superasse a marca de 500.000 toneladas. A perspectiva era que no mesmo ano o Brasil atingisse a autossuficiência, ou seja, satisfizesse por inteiro, as demandas internas(BIODIESELBR, 2018).

Tabela 1. Produtores mundiais de óleo de palma e estimativas das produções em 2019.

Posição	País	Toneladas	Produção mundial (%)
1º	Indonésia	43.000.000	56,72
2º	Malásia	21.000.000	27,7
3º	Tailândia	3.000.000	3,96
4º	Colômbia	1.680.000	2,22
5º	Nigéria	1.015.000	1,34
6º	Guatemala	852.000	1,12
7º	Equador	630.000	0,83
8°	Papoa Nova-Guiné	630.000	0,83
9º	Honduras	580.000	0,76
10º	Brasil	540.000	0,71
11º	Costa do Marfin	515.000	0,68
	Outros	2.372.000	3,13
	Total	**75.814.000**	**100,00**

Fonte: USDA (2019)

Cerca de 80% do óleo de palma produzido são utilizados na área alimentícia, aplicados em frituras, sorvetes, bolachas, chocolates, margarinas e gorduras especiais. Os outros 20%, são utilizados para finalidades não alimentícias como, produção de produtos farmacêuticos, lubrificantes, velas, sabonete, sabão, cosméticos e estudos no mundo todo estão sendo desenvolvidos visando sua aplicação na produção de biodiesel (LEVERMANN; SOUZA, 2014; KAWAZOS, 2014).

O fruto da palma é constituído por duas partes, a polpa vermelha, de onde se obtém o óleo de palma, e a amêndoa, que após prensagem origina o óleo de palmiste e para cada oito toneladas de óleo de palma bruto produzidas, cerca de uma tonelada de óleo de palmiste é produzida. Ambos poderão passar pelo processo de refino físico (branqueamento e desodorização). O óleo de palma refinado pode ainda passar pelo processo de fracionamento, originando a estearina e a oleína de palma (BASIRON, 2007)(KAWAZOS, 2014).

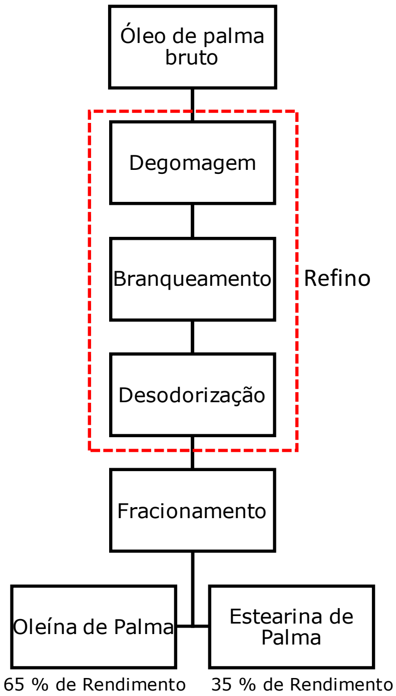
O processo de extração do óleo de palma é feito por prensagem mecânica e tem o seu refino feito com a adição de ácido cítrico ou fosfórico e água (degomagem) para remoção dos fosfolipídios não-hidrátáveis e hidratáveis, respectivamente, e metais, a uma temperatura de

90 a 100 °C. Em seguida, é feito o branqueamento com o auxílio de adsorventes para remoção de cor do óleo. E por último e mais importante etapa, a desodorização ou desacidificação tem por objetivo principal a remoção de odores indesejáveis, ácidos graxos livres e destruição de dos carotenoides e tocoferóis já que esse processo ocorre por destilação, com pressão absoluta de 3 mmHg e temperatura que variam de 240 a 260 °C, temperatura suficiente para degradar os carotenoides e tocoferóis e destilar os ácidos graxos livres(SILVA, 2007).

2.1.1 Oleína de Palma

A oleína de palma é um produto obtido através da operação de fracionamento em modo descontínuo ou batelada do óleo de palma refinado. Essa operação consiste em um resfriamento e agitação lenta, com a formação de pequenos cristais (estearina de palma) distribuídos de forma homogênea no volume ocupado do tanque. Do tanque de resfriamento o óleo é transferido com o auxílio de bombas para filtros prensa, onde, os cristais de estearina (fração sólida) ficam retidos, liberando a oleína de palma (fração líquida). Após filtração, um rendimento de aproximadamente 65 % de oleína de palma é obtido. A Figura 1 abaixo simplifica o processo de obtenção da oleína de palma (NUSANTORO, 2007).

Figura 1. Fluxograma simplificado das etapas de refino e fracionamento do óleo de palma.Fonte:Autor.



Conforme mostra a Tabela 2, o perfil de ácidos graxos da oleína de palma apresenta aproximadamente 36,00 % de ácido palmítico (C16:0), 46,60 % de ácido oleico (C18:1) e 10,20 % de ácido linoleico (C18:2), implicando em um óleo com quantidades majoritárias em ácidos graxos insaturados de cadeia longa (ALVA, 2016). A oleina de palma tende a apresentar características similares ao óleo de palma, apresentando apenas um percentual menor de ácido palmítico e uma maior quantidade de ácido oleico, o que possibilita um aspecto líquido a temperatura ambiente (ALVA, 2016 *apud* O'BRIEN, 2004).

Tabela 2. Perfil de ácidos graxos do óleo de palma e suas frações oleína e estearina de palma.

Óleo	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3
Óleo de palma	-	-	40,68	-	4,72	41,78	8,84	-
Oleína de palma	1,30	0,70	35,90	0,10	4,40	46,60	10,20	0,30
Estearina de palma	-	1,21	61,21	-	4,00	27,54	6,05	-

C12:0 = ácido láurico; C14:0 = ácido mirístico ; C16:0 = ácido palmítico; C16:1 = ácido palmitoleico; C18:0 = ácido esteárico; C18:1 = ácido oleico; C18:2 = ácido linoleico; C18:3 = ácido linolênico. Fonte: (MAGALHÃES et al., 2019)

O processo de fracionamento reduz as cadeias longas saturadas na fase líquida do produto obtido, e isso, dependendo do interesse, pode representar uma grande vantagem. Para utilização na produção de biodiesel, por exemplo, matérias-primas com menores quantidades de ácidos graxos saturados produzem ésteres etílicos ou metílicos com menor ponto de turbidez (CARDOSO et al., 2014).

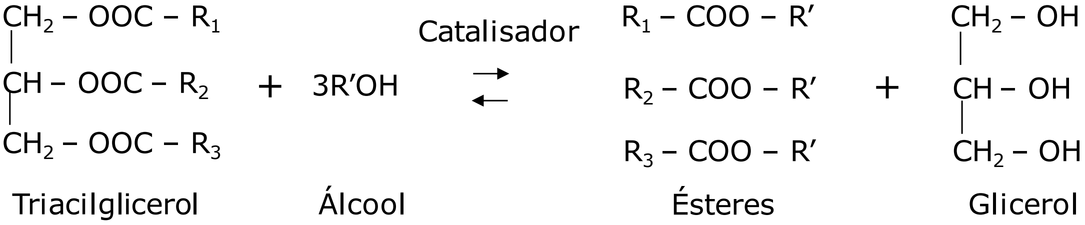
Porém, matérias-primas com maiores quantidades de ácidos graxos insaturados são mais susceptíveis às reações de oxidação provocadas pelo oxigênio, temperatura e presença de água (CARDOSO et al., 2014), sendo necessário o controle desses parâmetros para manter a qualidade do biodiesel por um período maior.

2.2 Reação de transesterificação

Geralmente, o biodiesel é produzido por meio da reação de transesterificação. Essa reação tem sido utilizada com o objetivo de reduzir a viscosidade dos triacilgliceróis, melhorando suas propriedades físicas para os motores a diesel (DEMIRBAS, 2009; MEHER; VIDYA SAGAR; NAIK, 2006).

A alcoólise, nome também dado a transesterificação, é a reação de um triacilglicerol presente em óleo vegetal ou gordura animal com um álcool (geralmente de cadeia curta) para formar ésteres graxos e glicerol. Como esta é uma etapa reversível, um excesso de álcool é usado para deslocar o equilíbrio da reação para o lado do produto. No entanto, é necessário a presença de um catalisador para acelerar a taxa de conversão e consequentemente o rendimento em ésteres alquílicos. A reação é mostrada na Figura 2 (MA; HANNA, 1999).

Figura 2. Reação de transesterificação de triacilglicerol com um álcool



Fonte: Fangrui Ma (1999)

A estequiometria da reação é de três moles de álcool para um de triacilglicerol (3:1). Porém, na prática é mais usual utilizar 6:1 para deslocar o equilíbrio para o lado do produto como descrito acima, e aumentar o rendimento em ésteres alquílicos (ENCINAR; GONZÁLEZ; RODRÍGUEZ-REINARES, 2007).

O processo de transesterificação pode ser afetado por diversos fatores, dependendo da condição de reação a ser utilizada. Os principais são: o tipo de óleo, o tipo de catalisador e a sua concentração, a relação molar de álcool:óleo e o tipo de álcool, a temperatura e o tempo de reação, e a intensidade de mistura ou velocidade de agitação do meio (MEHER; VIDYA SAGAR; NAIK, 2006).

2.3 Álcool

Além da escolha do éster, a escolha do álcool também é muito importante para produção do biodiesel (CARDOSO et al., 2014). Álcoois de cadeia curta como o metanol e etanol, são os mais aplicados na produção do biocombustível. O uso destes álcoois, embora apresentem algumas diferenças em relação à cinética de reação, proporcionam um rendimento final em ésteres praticamente inalterado. Com isso, a seleção do álcool é feita levando em conta principalmente o custo e o desempenho na reação (ENCINAR; GONZÁLEZ; RODRÍGUEZ-REINARES, 2007).

2.2.1 Metanol

O metanol é o álcool mais utilizado em reações para produção de biodiesel, devido à sua maior reatividade, baixo custo e disponibilidade (BOUAID; MARTINEZ; ARACIL, 2007; CARDOSO et al., 2014). Porém, esse álcool é altamente tóxico, podendo ser absorvido pela pele e é 100% miscível em água, ou seja, qualquer tipo de derramamento apresentaria sérios problemas ao meio ambiente (BOUAID; MARTINEZ; ARACIL, 2007).

2.2.2 Etanol

Com o intuito de se produzir um biocombustível 100 % oriundo de fontes renováveis e menos tóxico, o etanol, se apresenta como uma alternativa mais coerente para ser utilizada em reações de transesterificação. No Brasil, o seu uso pode ser justificado pelo fato do país ser um grande produtor de etanol, e isso pode acabar viabilizando sua utilização para produção de biodiesel. Além disso, a produção de ésteres etílicos ao invés de metílicos possui grande importância, porque permite a produção de um combustível com carbono extra oriundo da molécula de etanol, e este aumenta ligeiramente o poder calorífico e o número de cetano do biodiesel (CLARK, WAGNER, SCHROCK, PIENNAAR, & MAY, 1984 apud BOUAID et al., 2007).

Os ésteres alquílicos produzidos a partir da reação de etanólise apresentam também pontos de névoa inferiores aos dos ésteres metílicos, e este fato melhora o arranque de motores em regiões de climas frios (ENCINAR; GONZÁLEZ; RODRÍGUEZ-REINARES, 2007). Na Tabela 3, encontram-se algumas propriedades de biodiesel etílico e metílicos obtidos a partir da transesterificação do óleo de soja

Tabela 3. Propriedades de ésteres etílicos e metílicos

Propriedades	Éster etílico	Éster metílico
Viscosidade 40°C (cSt)	4,41	4,08
Densidade específica 15,6 °C	0,881	0,884
Poder calorífico (MJ/kg)	40,00	39,8
Número de cetano	48,2	46,2
Ponto de fluidez (°C)	- 4	-1
Ponto de nuvem (°C)	1	2
Ponto de fulgor (°C)	160	141
Enxofre (% mássica)	0,01	0,01

Fonte : (CLARK et al., 1984)

O grande inconveniente da utilização do etanol em reações de transesterificação é que em reações catalisadas por álcali há geralmente a formação de emulsões, que no caso da metanólise se decompõem rápida e facilmente para formar duas fases, uma rica em glicerol e outra rica em ésteres metílicos. Na etanólise, já não existe essa facilidade, pois as emulsões são mais estáveis e complicam a separação e purificação de ésteres, sendo este um dos maiores desafios enfrentados para a produção de éster etílico (ZHOU; KONAR; BOOCOCK, 2003). Além disso, o etanol possui outro inconveniente, que envolve o seu azeótropo (95,5 % de etanol e 4,5 % de água), e a presença de água em reações de transesterificação não é desejável, pois ocasiona na formação de produtos secundários e desativa sítios catalíticos, como serão apresentados nos itens a seguir.

2.4 Métodos catalíticos

2.4.1 Catálise homogênea

Na literatura, quantidades significativas de trabalhos envolvendo a produção de biodiesel por catálise homogênea foram relatadas.

Os catalisadores homogêneos podem ser ácidos ou básicos. Ácido sulfúrico e ácido clorídrico são comumente empregados como catalisadores ácidos, principalmente quando o óleo possui percentuais de ácidos graxos livres elevados (>1% em massa), esses catalisadores possuem a capacidade simultânea de esterificar e transesterificar os triacilgliceróis (ZABETI et al., 2009). No entanto, o processo requer uma alta razão molar de álcool para óleo e tempo de reação longo para converter o óleo em biocombustível (ZABETI et al., 2009; TIWARI; RAJESH; YADAV, 2018). Além disso, o ambiente ácido pode reduzir a vida útil do equipamento provocada pela corrosão (CANAKCI; VAN GERPEN, 1999).

A transesterificação utilizando catalisadores alcalinos como hidróxido de sódio e potássio (NaOH e KOH, respectivamente), quando comparados aos catalisadores ácidos ou heterogêneos, convertem os triacilgliceróis em biodiesel utilizando-se um menor tempo de reação, e condições reacionais amenas, como baixas temperaturas e menores percentuais de catalisador (ATABANI et al., 2012). No entanto, o seu uso apresenta alguns desafios que incluem separação e purificação dos produtos e não reutilização dos catalisadores (SANI; DAUD; ABDUL AZIZ, 2014). Para processos envolvendo a catálise por álcali são necessárias etapas especiais que tornem a matéria-prima adequada para reação. Óleos com altos percentuais de ácidos graxos livres (AGL) e água produzem grandes quantidades de sabão e mais água. O sabão que é produzido é removido com o glicerol ou é lavado com água. Quando o nível de AGL é superior a 5% o sabão inibe a separação dos ésteres e glicerol e contribui para a formação de emulsões durante a lavagem (GERPEN, 2005), propiciando assim um maior consumo de água e maiores custos para tratamento dessa água. Além disso, a água promove a hidrólise dos triacilgliceróis, produzindo novos ácidos graxos livres e diacilgliceróis (SANI; DAUD; ABDUL AZIZ, 2014). Portanto, as reações de transesterificação utilizando catalisadores alcalinos requerem matérias-primas refinadas, com concentrações de ácidos graxos livres e de água inferiores a 0,5% e 0,06% em massa, respectivamente, (ATABANI et al., 2012; WU et al., 2016).

Essas condições exigidas restringem o número de matérias-primas utilizadas para os processos homogêneos, visto que matérias-primas baratas, como óleo de cozinha e óleos ácidos necessitam de um pré-tratamento. Isso, somado ao tratamento de águas residuais geradas a partir das etapas de purificação do biodiesel e a perda dos catalisadores homogêneos podem provocar perdas financeiras e tornar o produto menos competitivo com o diesel comum (SANI; DAUD; ABDUL AZIZ, 2013).

Sendo assim, como forma de superar as dificuldades encontradas com a utilização de catalisadores homogêneos surge o uso dos catalisadores heterogêneos, que podem ser considerados benéficos à indústria por possuírem a facilidade de serem regenerados e reutilizados e não necessitam de um tratamento de água na etapa de separação (EVANGELISTA et al., 2016; DOSSIN et al., 2006).

2.4.2 Catálise heterogênea

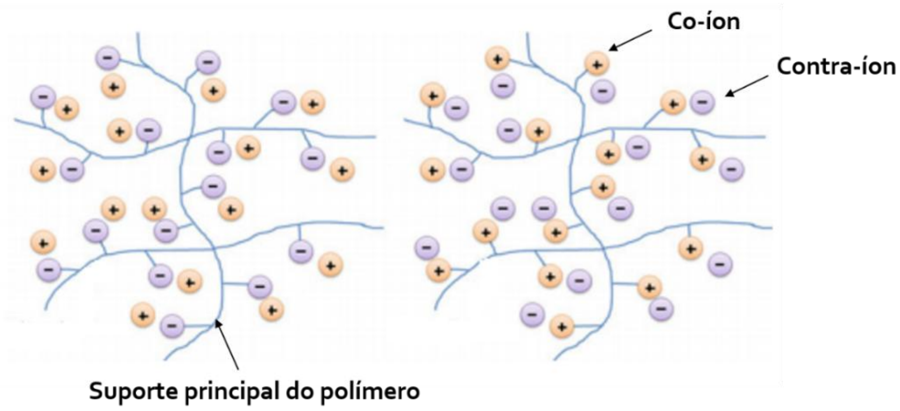
O principal foco dos recentes estudos para a produção de biodiesel está no desenvolvimento de catalisadores heterogêneos que possam ser reutilizados. Estes catalisadores foram propostos como uma forma benigna de substituir o uso dos catalisadores homogêneos ácidos e alcalinos (SANI; DAUD; ABDUL AZIZ, 2014).

As principais razões pelas quais os catalisadores heterogêneos têm recebido grande atenção está no fato deles serem não-corrosivos (FADHIL; AL-TIKRITY; KHALAF, 2018), podem ser regenerados, reutilizados, aplicados em processos contínuos (SHIBASAKI-KITAKAWA et al., 2011), e possuem facilidade de separação do produto obtido. Além disso, não possuem sensibilidade à ácidos graxos livres, elimina o passo de lavagem após a reação, visto que não produzem produtos secundários, como sabão. Diversos catalisadores heterogêneos têm sido estudados na literatura e, recentemente, as resinas de troca iônica chamaram bastante atenção por apresentarem condições favoráveis de reação, e possuírem a capacidade de transesterificar e purificar o produto simultaneamente através da adsorção de AGL.

2.4.2.1 Resina de troca iônica

Uma resina de troca iônica é um material insolúvel que retém e libera íons simultaneamente. A resina possui um grupo funcional responsável por fazer a permutação de íons. A estrutura insolúvel permite a difusão dos íons, e nesta estrutura deve conter uma matriz com uma carga iônica fixa, denominada co-íon. A neutralidade elétrica da estrutura é estabelecida quando existe um íon móvel de carga oposta ao íon fixo, chamados de contra-íons. Se a resina apresenta um complemento aniônico fixo insolúvel ela será um trocador catiônico, se a carga fixa for catiônica a resina será um trocador aniônico. Na Figura 3, em um trocador de cátions as cargas negativas fixas estão em equilíbrio com as cagas positivas livres que se movimentam nos interstícios do polímero, já para o trocador de ânions, ocorre o inverso (NASEF, UJANG, 2012).

Figura 3. Diagrama dos trocadores catiônicos (esquerda) e aniônicos (direita)



Fonte: Nasef e Ujang (2012)

As resinas catiônicas atraíram recentemente bastante atenção por apresentar condições reacionais suaves, não provoca corrosão em equipamentos e possui elevada concentração de locais ativos e menor produção de águas residuais. Esses catalisadores possuem numerosos sítios ácidos ativos que são utilizados para reações de esterificação (MA et al., 2015; RODRIGUES; PASA; CREN, 2018). Já as resinas aniônicas são conhecidas por facilitarem a transesterificação de óleos e podem ser classificadas em fracamente básicas, quando formadas pelo grupo funcional de aminas terciárias, ou fortemente básicas, quando apresentarem o grupo funcional de quaternário de amônio (JAMAL; RABIE; BOULANGER, 2015; NASEF, UJANG, 2012).

Na ação de troca iônica são muitos os fatores que exercerão influência forte no processo, e estes estão diretamente relacionados com a resina (fase sólida) e a solução a ser tratada (fase líquida) (CREN, 2009). O tamanho da partícula, a porosidade, a capacidade, a seletividade, o grau de *crosslinking,*ou seja, o grau de interligações entre os polímeros da matriz, o efeito *swelling* (encharcamento provocado pela presença de solvente nos poros), a estabilidade, as propriedades eletrostáticas da resina e o solvente de contato são características que desempenham função importante no processo de permuta iônica. (CREN, 2009 apud HELFFERICH, 1962 e DOFNER, 1991).

Segundo Cren (2009), para que o processo de troca iônica entre um sólido e uma solução ocorra é necessário que certos critérios sejam atendidos, como:

- Deve ser usado um solvente, onde a espécie a trocar íons é solúvel;
- Deve haver íons pelo menos parcialmente dissociados ou ionizados em ambas as fases (sólido e líquido);
- Os íons devem possuir livre caminho para se movimentar e trocar de lugar um com o outro;
- E por último, a dissolução ou dissociação do sólido da resina de troca iônica jamais deve ocorrer.

2.4.3 Catálise enzimática

Enzimas são proteínas que atuam como catalisadores e são geralmente extraídas de fungos e bactérias. Reações de transesterificação catalisada por enzimas possuem vários benefícios quando comparada com a transesterificação em meios homogêneos, pois apresenta uma conversão completa de matérias-primas com alto teor de AGL e água sem que ocorra formação de sabão (MURILLO et al., 2018). Porém, a tecnologia enzimática para produção de biodiesel ainda esbarra no alto custo de produção da enzima lipase e em sua instabilidade (ADEWALE; DUMONT; NGADI, 2016; MEHER; VIDYA SAGAR; NAIK, 2006).

2.5 Produção de ésteres alquílicos utilizando resina de troca iônica

As resinas de troca aniônica têm sido estudadas em diversos trabalhos objetivando a conversão de triacilgliceróis (T) em ésteres alquílicos (E). Segundo Shibasaki-Kitakawa et al.(2007) na reação de alcoólise, o primeiro passo para a resina de troca aniônica ($S(OH^-)$) é a adsorção do álcool (A) no catalisador da resina, conforme mostra a Figura 4, onde D é o diacilglicerol, M é o monoacilglicerol e G é o glicerol.

Figura 4. Mecanismo de reação utilizando resina de troca aniônica

$$A + S(OH^-) \rightleftarrows A^- + S(OH)^- - H^+$$

1° etapa $$A^- + T \rightleftarrows AT^-$$

$$AT^- \rightleftarrows E + D^-$$

$$D^- + S(OH^-) - H^+ \rightleftarrows D + S(OH)^-$$

2° etapa $$A^- + D \rightleftarrows AD^-$$

$$AD^- \rightleftarrows E + M^-$$

$$M^- + S(OH^-) - H^+ \rightleftarrows M + S(OH)^-$$

3° etapa $$A^- + M \rightleftarrows AM^-$$

$$AM^- \rightleftarrows E + G^-$$

$$G^- + S(OH^-) - H^+ \rightleftarrows G + S(OH)^-$$

Fonte: Adaptado de Shibasaki – Kitakawa et al. (2007)

Shibasaki-Kitakawa et al. (2007) citaram ainda que a força de adsorção na resina era muito maior para o álcool do que para o éster, apresentando o comportamento oposto das resinas de troca catiônica que mostraram uma força maior para adsorver primeiro os ácidos graxos. Por essa razão, os autores afirmam que resinas de troca aniônica mostraram uma atividade maior que as resinas de troca catiônica para converter triacilgliceróis em biodiesel. Avaliando diferentes resinas, eles observaram que as do tipo porosa, Diaion PA308, PA306 e PA306S (Mitsubishi Chemical Co., Ltd., Japão), apresentaram taxa de conversão superiores as da resina do tipo altamente porosa (HPA25). A resina PA306S com menor densidade de *crosslinking* e tamanho de partícula proporcionaram uma maior taxa de reação, com uma conversão de 80% em ésteres etílicos. Assim, foi observado que essas duas características possuem um efeito maior sobre a taxa de reação em comparação com a porosidade. Segundo Rios et al. (2005) uma maior densidade de *crosslinking* (teor maior de divinilbenzeno) diminui a propriedade de inchamento da resina, dessa forma, os sítios catalíticos ficam menos acessíveis ao substrato (RIOS et al., 2005).

Na literatura, também se tem estudado a resistência da resina à água. Utilizando a resina aniônica D261,com o grupo funcional amônio quaternário Ren et al. (2012) observaram que a conversão em ésteres metílicos diminuiu de 95,2% para 87,7% com o teor de água aumentando de 0,0 % para 1,0 % em massa. Segundo os autores, a água pode desativar os sítios ativos catalíticos OH^-, porque as moléculas de água se ligam mais efetivamente aos sítios ativos do que o metanol.

Paterson et al. (2013), avaliando a resina catiônica Amberlyst 15 (Alfa Aesar Co., Ward Hill, USA) e adicionando percentuais de água na matéria-prima em até 1,0 % em massa, não observaram efeitos nos produtos de reação medidos por HPLC (com0,1 %, 0,5 % e 1,0% foram obtidas conversões de 95,8%, 95,2% e 96,3%, respectivamente). Com2,0 % em massa, já se conseguiu verificar uma diminuição na conversão para produtos (92,6 % de conversão).

Deboni et al. (2018), utilizando óleo de soja com etanol e a resina Amberlyst A26 OH (The Dow Chemical Company) em experimentos preliminares, observaram que a presença de água no interior da resina diminuiu a taxa de reação. Como forma de superar esse problema um pré-tratamento por condicionamento com etanol foi adicionado ao processo, visando eliminar a água presente na resina. Avaliando simultaneamente a remoção de AGL e a produção de biodiesel, Deboni et al. (2018) também observaram que é possível desacidificar a matéria-prima e produzir biodiesel simultaneamente, desde que grandes quantidades de resina sejam utilizadas (20 % em base seca de resina em relação a massa de óleo), pois no processo de adsorção dos ácidos graxos livres os sítios ativos são ocupados pelos AGL. Quantidades de resina acima da concentração de saturação dos sítios ativos devem ser utilizadas visando disponibilizar sítios catalíticos para a transesterificação. Além disso, os autores afirmam que a adição desnecessária de solvente pode ser evitada levando-se em conta o teor de álcool presente na resina oriunda do condicionamento.

Alva (2016) em seu trabalho utilizando a resina Amberlyst A26 OH como catalisador heterogêneo e, óleo e oleina de palma como fonte de triacilglicerol, encontrou conversões em ésteres etílicos de 87,1 % e 81,5 %, respectivamente. Estas conversões foram encontradas utilizando uma concentração de catalisador de 10 %, temperatura de 71 °C, razão molar de óleo:etanol de 1:9,3 e agitação de 400 rpm durante 8 horas de reação (ALVA, 2016). Alva observou através da análise do planejamento experimental que quanto maior a temperatura e menor a razão molar oleína:etanol, maior é a conversão. O autor ainda citou, que, a porcentagem de catalisador tem uma influência positiva na reação, mas um excesso na quantidade provoca uma diminuição na conversão.

Outras informações envolvendo o uso de resinas de troca iônica, assim como outros catalisadores heterogêneos, para uso na produção de biodiesel, são mostradas no capítulo 3.

CAPÍTULO 3

Heterogeneous Catalysts for Biodiesel Production: A Review

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Heterogeneous Catalysts for Biodiesel Production: A Review

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Abstract Biodiesel is a biofuel and appears on the world energy scene as a strong substitute for petroleum diesel for its renewable and less environmentally polluting character. It can be obtained from transesterification reaction of triacylglycerol from vegetable oils or animal fats with short chain alcohol in the presence of homogeneous or heterogeneous catalysts. In recent years the production of alkyl ester by using heterogeneous catalysts it has excelled due to their capacity for regeneration, reuse and reduction of processing stages. Several parameters have been evaluated in the reaction steps, such as amount of catalyst, molar ratio of alcohol:oil, temperature, agitation speed and reaction duration. Intrinsic properties of catalysts are also studied, such as porosity, surface area, catalytic activity and others. Therefore, this review presents the transesterification reaction of several raw materials, as sources of triacylglycerols, using short chain alcohols and different heterogeneous catalysts. Optimal conditions for each catalyst, as well as its respective reaction mechanisms, were summarized.

Keywords anion exchange resin, alkaline earth oxides, hydrotalcites.

1. Introduction

It is already quite evident that combating climate change needs urgent modifications in the way energy is generated and the replacement of fossil energy resources by renewable energies is very necessary [1].

Biodiesel appears in the bioenergy scenario as a good source in substitution of fossil fuels and has become a very relevant research topic due to its wide use in the energy and transport sector [2]. In the last 10 years more than 28,000 studies related to the production and consumption of biodiesel have been published on online research platforms, thus confirming what was said by Boloy et al. (2017) [2].

According to projections of the International Energy Agency, the production of biofuels will increase by 3.3 million barrels/day from 2012 to 2040 and its share will be 8% in demand for road transport fuels [3]. Therefore, due to renewable energy requirement, biodiesel will likely play an important function in increasing fuel demand in the coming decades. [4].

Different raw materials, sources of triacylglycerols, are used for biodiesel production. The most used are: soybean oil [5], rapeseed oil [6], canola oil [7], palm oil [8], cottonseed oil [9], *Jatropha curcas* oil [10], used cooking oil [11], and animal fats [12,13]. Vegetable oils used in transesterification reactions for the production of biodiesel depend mostly on crops adapted to the regional or local climate. An example, in the United States, the soybean oil is the most commonly used triacylglycerol source for alkyl ester production, while in Europe and in warmer climate countries, rapeseed oil and palm oil are more common, respectively. [14,15]. Whenever possible, the raw materials for biodiesel production must meet two conditions, one is the low cost of production and another one is the large scale of production [14], which makes its process economically viable and a competitive fuel to petroleum diesel. Conventionally, the biodiesel is obtained via transesterification of vegetable oils or animal fat. In the reaction, a triacylglycerol molecule, the main component of vegetable oils, reacts with three molecules of a short chain alcohol, normally, methanol or ethanol, in the presence of a catalyst. Producing three molecules of fatty acid methyl or ethyl esters (FAME or FAEE, respectively) and one molecule of glycerol [16].

Distinct catalysts are used to accelerate the transesterification reaction, and can be classified into homogeneous and heterogeneous catalysts.

The homogeneous catalysts used for the alcoholysis reactions may be acid or basic in nature. Industrially, basic catalysts are more commonly applied for biodiesel production. This is because the base catalyzed reaction is faster than the acid catalyzed reaction. In addition, the yield in fatty acid alkyl esters is higher and reaction conditions are relatively mild. However, the choice of this catalyst is dependent on the amount of free fatty acids (FFA) and the concentration of moisture present in the raw material [17].

The homogeneous catalysis systems have many disadvantages, such as the difficulty in separating the catalyst from the glycerin phase and the need to use a large amount of water in the purification of biodiesel, generating a large amount of wastewater.

Other considerable disadvantages of homogeneous catalysts are that they cannot be reused and their separation is difficult because the catalyst is dissolved in the reagents and requires specialized types of equipment for their recuperation that can result in increased process costs [18,19].

Thus, in order to overcome the disadvantages mentioned above, the heterogeneous catalysts have emerged as a viable substitute for homogeneous catalysts [20].

Heterogeneous catalysts are not dissolved in the reaction medium, thus, being separated easily from the reaction mixture. As advantage, the products contain less impurities and the purification costs from biodiesel are reduced [18]. These catalysts also have two beneficial advantages for industry and the environment because they can be easily regenerated and reused. Thus, they can be considered ecologically correct, since they do not require water treatment in the separation stage [21]. These advantages simplify washing, separation and purification processes after the reaction and there is no soap formation in the process [18].

With that, this article aimed to study the reaction mechanisms of the different types of solid heterogeneous catalysts, the optimum conditions and catalytic efficiency.

2. Homogeneous catalysis

In the literature, significant amounts of studies involving the production of biodiesel by homogeneous catalysis have been reported.

The homogeneous catalysts can be acids or bases. Sulfuric acid and hydrochloric acid are the most employed as acid catalysts, especially when the oil has elevated percentages of FFA (> 1% by mass), these catalysts have the simultaneous ability to esterify and transesterify the triacylglycerols [20]. However, the process requires a high molar proportion of alcohol to oil and reaction time more larger to convert the oil into biodiesel [20,22]. Moreover, the acid environment can reduce the life of the equipment caused by corrosion [23].

The transesterification using alkaline catalysts as sodium and potassium hydroxide (NaOH and KOH, respectively), although have a high conversion percentages, faster reaction rate and moderate reaction conditions [24], they still have challenges that include separation and purification of products and non-reuse of catalysts [25]. For processes involving alkali catalysis, special steps are required to make the raw material suitable for reaction. Oils with high percentages of FFA and water produce large amounts of soap and more water. The soap that is produced is removed with glycerol or washed with water. When the FFA amount is higher than 5%, the soap makes it difficult the separation of the esters and glycerol and contributes and assists in emulsion formation during washing [26], thus providing, a greater water consumption and higher costs for the treatment of this water. In addition, the water promotes the hydrolysis of triacylglycerols, producing new free fatty acids and diacylglycerols [25]. Therefore, the transesterification reactions using alkaline catalysts require refined raw materials, with concentrations of free fatty acids and water lower than 0.5% and 0.06% by mass, respectively [24,27].

These conditions restrict the number of raw materials used for homogeneous processes since cheap raw materials such as cooking oil and acid oils require a pretreatment. This, coupled with the treatment of wastewater generated from the biodiesel purification stages and the loss of the homogeneous catalysts can cause financial losses and make the product less competitive with the petroleum diesel [28].

Thus, as a way of overcoming the difficulties encountered with the use of homogeneous catalysts, the use of heterogeneous catalysts appears to be more beneficial to the environment and industry because they have the facility of being regenerated and reused and do not require a water treatment at purification steps [18,21].

3. Heterogeneous catalysis

The main focus of the recent studies on biodiesel production is the development of heterogeneous catalysts that can be reused. These catalysts were proposed with an advantageous form of replacing the use of acidic and alkaline homogeneous catalysts [25].

The main reasons by which heterogeneous catalysts have received great attention is the fact that they are non-corrosive [29], can be regenerated, reused, applied in continuous processes [30], and have easy separation of the obtained product. In addition, they lack sensitivity to free fatty acids, the washing step is eliminated, since they do not produce side products such as soap [25].

Thus, several heterogeneous solid catalysts have been studied. Calcium and magnesium oxides [31,29,32,33,34,35,36,37,38,39,40], hydrotalcites [41,42,43,44] and ion exchange resins [45,46,47,48,49,50,51,52,53] were studied in the yield of the transesterification reaction, as shown in Table 1.

Table 1: Reaction conditions using different heterogeneous catalysts and their respective yields on methyl and ethyl esters

Catalyst	**Oil**	**Alcohol**	**MR A:O^{A}**	**Ratio catalyst/Oil (w/w)**	**Temperature (°C)**	**stirring speed (rpm)**	**Time (h)**	**Conversion (%)**	**Reference**
CH_3CO_2K/ CaO	Bitter almond oil	Methanol	9:1	2.0 %	60 °C	600	2.0 h	91.22 %	[29]
CaO/SiO_2	Cooking oil	Methanol	14:1	8.0 %	60 °C	-	1.5 h	91 %	[32]
Mayenite impregnated with 10% lith	Refined rapeseed oil	Methanol	6:1	5.0 %	60 °C	180	2.0 h	100 %	[33]
Na_2ZrO_3	*Ricinus communis* oil	Methanol	15:1	5.0 %	65 °C	-	3.0 h	99.9 %	[54]
MgAl hydrotalcites containing K (HTCRk)	Sunflower oil	Methanol	3:10^{B}	3.0 %	65 °C	200	3.0 h	>80 %	[41]
MgO supported on γ-Al_2O_3	Soybean oil	Methanol	6:1	5.0 %	60 ºC	-	6.0 h	60 %	[37]
$MnCO_3$	Soybean oil	Subcritical methanol	21:1	2.0 %	180 ºC	200	1.0 h	98.1 %	[55]
Potassium methoxide	Soybean oil	Methanol	6:1	2.0 %	80 °C	-	0.25 h	91 %	[56]
Mixed oxide of Ca and Li ($CaLiZrO_3$)	Soybean oil	Ethanol	12:1	10 %	50 °C	1100	0.5 h	92 %	[57]

Mixed oxide of Ca and Al derivative of (Ca_2Al-c)	Macaúba oil	Ethanol	14:1	3.0 %	65 °C	600	12 h	91 %	[58]
Hydrotalcite –hydroxyapatite doped with nano carbon tubes	Soybean oil	Methanol	12:1	2.5 %	240 °C	700	4.0 h	40.5 %	[44]
Hydrotalcite –hydroxyapatite	Soybean oil	Methanol	12:1	5.0 %	240 °C	700	4.0 h	80.4 %	[43]
Hydrotalcite - Ga^{3+}	Soybean oil	Ethanol	20:1	20 %	120 °C	-	12 h	75.5 %	[59]
Hydrotalcite of Mg/Al	Cooking oil	Methanol:ethanol (4:2)	6:1	1.5 %	80 °C	300	2.5 h	95.2 %	[42]
Zn/Ca/Al2O3	Cooking oil	Methanol	24:1	6.0 %	65 °C	-	3.0 h	97.8 %	[11]
Molecular sieve AL-SBA-15	*Jatropha curcas* oil	Methanol	12:1	6.5 %	180 °C (4MPa)	400	24 h	>99.0 %	[60]
Amberlyst- A26 OH	Canola oil	Methanol	6:1	3.0 %	45 °C	1000	1.5 h	67 %	[61]
Amberlyst- A26 OH	Canola oil	Ethanol	6:1	3.0 %	45 °C	1000	1.5 h	63 %	[61]
D261 anion exchange resin	Soybean oil	Methanol and n-hexane^{C}	9:1	80 g^{E}	50 °C	-	0.92 h	95,2 %	[62]
D261 anion exchange resin	Soybean oil	Methanol and n-hexane^{D}	9:1	80 g^{E}	50 °C	-	0.92 h	96,7 %	[62]
Diaion PA306S resin	Triolein	Ethanol	10:1	40 %	50 °C	-	3.0 h	80 %	[63]
Diaion PA306S resin	Cooking oil	Methanol	3,5:1	50 %	50 °C	-	10 h	>90 %	[30]

Amberlyst-A26 OH	Tallow fat	Methanol	6:1	2,2 mol/ L	65 °C	-	8.33 h	>95 %	[64]
Amberlyst-A26 OH	Soybean oil	Ethanol	16:1	20 %	50 °C	500	6.0 h	>99 %	[65]
Amberlyst-A26 OH	Soybean oil	Methanol	10:1	20 %	50 °C	550	18 h	not reported	[48]
Diaion PA306S resin	Acid rice bran oil	Methanol	-	33 %	50 °C	-	40 h	97.1 %	[53]

[A]Molar ratio of alcohol:oil (A:O); [B]The author used a methanol/oil mass ratio of 3:10; [C]n-hexane/soybean oil weight ratio of 0.5; [D]n-hexane/soybean oil weight ratio of 0.9

[E]Fixed bed reactor loading with 80 g of resin and feedstock flow rate of 1.2 ml/min for 0,92 hours

3.1. Ion Exchange Resin

An ion exchange resin is an insoluble solid material that has the ability to retain and release ions simultaneously. The resin has a functional group responsible for permutation of ions. The insoluble structure allows the diffusion of the ions, this is, the solid must contain a fixed ionic charge, called counterion. The electrical neutrality of the structure is achieved when there is a mobile ion of ionic charge opposite to the fixed ion. If the resin has a fixed anionic insoluble complement it will be a cation exchanger, if the fixed charge is cationic the resin will be an anion exchanger [66].

Recently, the cationic resins attracted a great deal of attention due to the soft reaction conditions, non corrosion in the equipment, a high concentration of active sites and lower residual waters production. These catalysts have numerous active acid sites that are used for esterification and transesterification reactions [67,51]. Therefore, in this review, only the use of anion exchange resins will be addressed, since, for biodiesel production, they have applications only in transesterification reactions.

3.1.1. Anion Exchange Resin

The anion exchange resins have been studied by several researchers in the conversion of triacylglycerols (T) to fatty acid alkyl esters (E). According to Shibasaki-Kitakawa et al. (2007)[63] in the transesterification reaction, the first step of the reaction is the adsorption of the alcohol at the active site of the ion-exchange resin ($S(OH^-)$) with formation of an alkoxide (A^-) and an H^+ ion. The formed alkoxide attacks the triacylglycerol (T) molecule, thereby producing a fatty acid alkyl ester (E) molecule and an ionized diacylglycerol (D-) molecule. The negatively charged diacylglycerol undergoes an electrophilic addition with the H^+ ion to form the neutral diacylglycerol (D). In the second step, occurs the formation of the second alkyl ester molecule from the nucleophilic attack of A^- to the diacylglycerol, forming, in addition to the alkyl ester, a monoacylglycerol (M) molecule. In the third step, the formation of the third alkyl ester molecule and the production of a glycerol (G) molecule take place.

According to the authors, in the proposed mechanism, during the reaction, the resin has the regeneration capacity, maintaining its active catalytic sites.

Shibasaki-Kitakawa et al. (2007)[63] also reported that the adsorption force on the resin was much higher for the alcohol than for the triacylglycerols, exhibiting the opposite behavior of the cation exchange resins that showed a greater force to adsorb first the fatty acids in esterification reaction. For this reason, the authors state that anion exchange resins showed greater activity than cation exchange resins to convert triacylglycerols to biodiesel. Evaluating the different types of resin, the authors observed that the porous type Diaion PA308, PA306 and PA306S (Mitsubishi Chemical Corporation, Japan) presented higher conversion rates than the highly porous type resin Diaion HPA25 (Mitsubishi Chemical Corporation, Japan). Diaion PA306S resin with lower *cross-linking* density and particle size provided a higher reaction rate, with 80 % conversion to ethyl esters using an expanded bed column with recirculation system packaged with 40% resin in relation to the mass of oil and a molar ratio of ethanol and triolein of 10:1, during 3 hours of reaction at a temperature of 50 °C. Thus, it was observed that these two characteristics had greater influence on the reaction rate when compared to resin porosity. According to Rios et al. (2005)[68] a higher *cross-linking* density (higher divinylbenzene content) decreases the resin swelling property, thus, the catalytic sites stay less accessible to the substrate [68].

1° step

$$A + S(OH^-) \rightleftarrows A^- + S(OH)^- - H^+$$

$$A^- + T \rightleftarrows AT^-$$

$$AT^- \rightleftarrows E + D^-$$

2° step

$$D^- + S(OH^-) - H^+ \rightleftarrows D + S(OH)^-$$

$$A^- + D \rightleftarrows AD^-$$

$$AD^- \rightleftarrows E + M^-$$

3° step

$$M^- + S(OH^-) - H^+ \rightleftarrows M + S(OH)^-$$

$$A^- + M \rightleftarrows AM^-$$

$$AM^- \rightleftarrows E + G^-$$

$$G^- + S(OH^-) - H^+ \rightleftarrows G + S(OH)^-$$

Figure 1. Mechanisms of anion exchange resin reaction. Source: Adapted from Shibasaki-Kitakawa et al.(2007) [63]

In the literature, the resistance of the resin to water has also been studied. Using the Nankai D261 anionic resin (Chemical Nankai, Japan) commercialized in Cl^- form with quaternary ammonium functional group, Ren et al. (2012) [62] found that conversion to methyl esters reduced from 95.2% to 87.7% with water content heightened from 0.0% to 1.0% by mass of oil. According to the authors, water can deactivate the active sites OH^-, it happens because water molecules bind more effectively to catalytic sites than methanol. Peterson et al. (2013) [50], evaluating the Amberlyst 15 resin (Alfa Aesar Co.,USA) by adding water up to 1.0% by mass, observed no significant effects on the reaction products measured by HPLC (0.1%, 0.5% and 1.0% of water, the conversions were of 95.8%, 95.2% and 96.3%, respectively). At 2.0% by mass, a reduction in the conversion to products (92.6%) was verified.

Deboni et al. (2018) [65], using soybean oil with ethanol and Amberlyst A26 OH resin (Dow Chemical Company, USA) in preliminary experiments, observed that the presence of water inside the resin decreased the reaction rate. As a way of overcoming this problem, a pretreatment by conditioning the resin with ethanol was added to the process with the aim of eliminate the water present in the resin.

Evaluating simultaneously the removal of FFA and the production of biodiesel Deboni et al. (2018) [65] observed that it is possible to deacidify the raw material and produce biodiesel simultaneously, since large amounts of resin are used, because the adsorption of the free fatty acids deactivated the sites. Quantities of resin above the saturation concentration of the active sites should be used in order to provide catalytic sites for the transesterification. In addition, the authors state that the unnecessary addition of solvent can be avoided by taking into account the alcohol content present in the resin from its conditioning.

3.2. Alkaline Earth Oxide Catalysts

Several studies have been reported in the literature using alkaline earth oxides as heterogeneous catalysts of the transesterification reaction. Recently, studies involving the use of CaO, MgO and CaO impregnated with silica or potassium acetate have been reported in the literature [39,21,38,29,32].

Sousa et al. (2018) [39] studied the commercial CaO and CaO obtained from the calcination of eggshells as catalysts and obtained a 96% conversion to fatty acid methyl esters (FAME) for both of them using a soybean oil: methanol molar ratio of 1:12 , 3% (w/w) catalyst and a temperature of 65 °C for 4 hours of reaction under stirring at 600 rpm. In addition, a study was realized to verify if the catalyst was leached to the liquid phase, causing a homogeneous catalytic reaction. In this case, the authors observed that after the removal of the solid phase the conversion to methyl esters ceased, confirming that reaction is a heterogeneous catalytic one, since, the FAME contents did not increase after the removal of the solid catalyst [39].

A study of Putra et al.(2018) [32] involving the use of CaO doped with SiO_2 provided a greater conversion due to an increase in the surface area of the catalyst caused by SiO_2 impregnation. Using only CaO, 71% of conversion to methyl esters was obtained. After impregnation, the percentage increased to 91%. This fact was also caused by the possible process of esterification of the FFA caused by the presence of silica, a material with a high acidity that facilitates the esterification reaction, as shown in Figure 2, where in the first step the SiO_2 is responsible for attracting the FFA to its active site. In the second step, the hydroxyl (-OH) of methanol binds to O of the catalyst, and thereby, releases H_2O by the catalyst. In the third step, according to the author, CH_3 is incorporated into the O atom to form the fatty acid methyl ester.

After two cycles of use of the catalyst, a reduction of only 2% in biodiesel conversion was observed [32]. In addition, Putra et al. (2018) [32] propose that the reaction mechanism for transesterification has as its first step the adsorption of triacylglycerol and soon after the methanol, both react on the surface of the catalyst producing the biodiesel, as shown in Figure 3.

In this mechanism, CaO first interacted with triacylglycerol, as shown in the first step of the reaction. According to the author, triacylglycerol bounds to CaO forming a Ca and O-CH_2 bond. The presence of the -CH_2 aliphatic group was determined by FTIR of the catalyst. For the authors this revealed the existence of triacylglycerols on the surface of the catalyst, confirming the theory that before reacting with the methanol, the catalyst reacted with triacylglycerols. In step 2, the excess methanol disrupted the interaction of the triacylglycerol with the catalyst. Thus, CH_3O^- of methanol would replace the O^- position in the catalyst to form the biodiesel, so the methyl ester was released of the surface as shown the step 2. In the third step glycerol formation occurs and its desorption from catalyst surface.

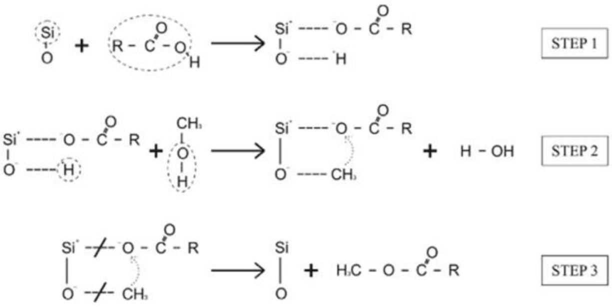

Figure 2. Mechanisms proposed by Putra et al. (2018)[32] for esterification reaction

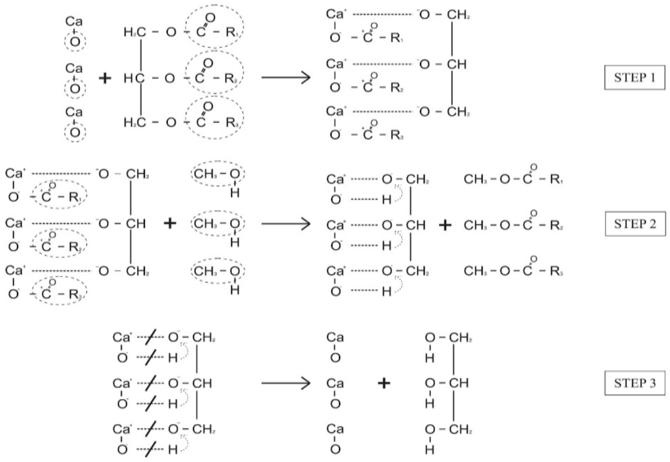

Figure 3. Mechanisms proposed by Putra et al. (2018)[32] for transesterification reaction

Unlike CaO, for MgO, Dossin et al. (2006)[21] proposed by Eley-Rideal kinetic model that the limiting step of the process is the adsorption of methanol at the active sites of the catalyst, ie, the reaction does not start without the adsorption of methanol in the catalyst. The mechanism was similar to that proposed for anion exchange resins and different from that mentioned for CaO by Putra et al.(2018)[32].

Navas et al. (2018)[37] studied the transesterification of soybean oil using methanol as solvent and MgO and CaO in bulk and doped with γ-Al_2O_3 as heterogeneous catalysts [37]. For the catalysts formed only by Ca or Mg, the conversions observed were of 38% and 13%, respectively. For the supported catalysts the conversions were 55% and 60%, respectively. According to these authors, the presence of the alumina improved the dissociation of the methanol in CH_3O^- and H^+, which occurs in the basic surface of the catalyst. In a first step, the methanol is adsorbed on the surface of the solid and the H^+ ion is abstracted from the methanol molecule to form a methoxide anion, the second step consists of the anion attack to the carbonyl carbon to generate an alkoxycarbonyl intermediate, which dissociates to form a fatty acid methyl ester and anionic diacylglycerol. This anion is attracted by a cation of the methoxide to form a diacylglycerol. The reaction is repeated twice to form monoacylglycerol and glycerol [37]. In his study, Navas et al. (2018)[37] show schematically the mechanism of reaction mentioned.

Fadhil et al. (2008)[29] also observed a loss in the catalytic activity of CaO doped with potassium acetate, a gradual decrease with the use was observed reaching 75% conversion in the 4th cycle. They attributed this decrease to the leaching of the active metals from the catalyst surface, as well as a change in the surface of the solid caused by washing and recalcination for the regeneration of the catalyst. In addition, the deactivation of the active sites may have been caused by the adsorption of oil, glycerol and free fatty acids on the surface of the catalyst, thus reducing the active sites.

3.3. Catalysts based on Hydrotalcite

Hydrotalcite (HT) is a double hydroxide, which can be found in its natural or synthetic form, contains in its structure interlayers of anionic species. The hydrotalcites are within the category of basic anionic clays and their general formula is given by $[M^{2+}_{(1-x)}\ M^{3+}_{x}(OH)_2]^{x+}\ A^{m-}_{x/m} nH_2O$, where M^{2+} is the divalent metal cation, M^{3+} is the trivalent metal cation, A^{m-} is the compensation anion, x is the molar ratio $M^{3+}/(M^{2+} + M^{3+})$ and *n* is the degree of hydration [43][69]. Several studies involving catalysts based of hydrotalcites to produce biodiesel via transesterification are available in the literature [69,70,71,72,73,74,75,76].

Three kinetic mechanisms, Eley-Ridal (ER), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Hattori were studies by Kapil et al. (2011)[77] based on pseudo-stationary states for surface reaction and methanol adsorption as limiting steps in the conversion rate for biodiesel production using triacylglycerols and methanol in the presence of different heterogeneous catalysts based on hydrotalcites ($Mg_{0,81}Al$; $Mg_{1,38}Al$; $Mg_{1,62}Al$ and $Mg_{2,93}Al$).

In the ER mechanism, for modeling the adsorption of methanol in the active sites was considered, forming the methoxide and reacting with triacylglycerols, diacylglycerols and monoacylglycerols, thus producing methyl esters and glycerol.

In the LHHW kinetic mechanism the first step is the adsorption of methanol with the subsequent adsorption of triacylglycerol. The main difference between the ER and LHHW model is the adsorption of triacylglycerols on the surface of the catalyst. Both adsorbed compounds react with each other on the surface of the solid to form diacylglycerol and methyl ester. Subsequently, the adsorbed methanol reacts with diacylglycerol and monoacylglycerol to form biodiesel and glycerol. Jamal et al. (2015), in their study on determining reaction constants, described the reaction steps considered in ER and LHHW kinetic reaction models, as shown in Table 2. In addition, the authors considered the effect of FFA adsorption on reaction kinetics, more details can be observed in the item kinetic models.

Table 2. Steps considered for the ER and LHHW models

Reaction step	ER model	LHHW model
Methanol adsorption	$MeOH +* \underset{K-1}{\overset{K\ 1}{\rightleftarrows}} MeOH *$	$MeOH +* \underset{K-1}{\overset{K\ 1}{\rightleftarrows}} MeOH *$
Triacyglycerol adsorption	Not exist	$T +* \underset{K-2}{\overset{K\ 2}{\rightleftarrows}} T *$
Surface reactions	$T + MeOH * \underset{K-2}{\overset{K\ 2}{\rightleftarrows}} E + D$ $*$ $D + MeOH * \underset{K-3}{\overset{K\ 3}{\rightleftarrows}} E + M$ $*$ $M + MeOH * \underset{K-4}{\overset{K\ 4}{\rightleftarrows}} E + G$ $*$	$T * +MeOH * \underset{K-3}{\overset{K\ 3}{\rightleftarrows}} E * +D *$ $D * +MeOH * \underset{K-4}{\overset{K\ 4}{\rightleftarrows}} E * +M *$ $M * +MeOH * \underset{K-5}{\overset{K\ 5}{\rightleftarrows}} E * +G *$
Desorption	$D +* \underset{K-5}{\overset{K\ 5}{\rightleftarrows}} D *$ $M +* \underset{K-6}{\overset{K\ 6}{\rightleftarrows}} M *$ $G +* \underset{K-7}{\overset{K\ 7}{\rightleftarrows}} G *$	$E +* \underset{K-6}{\overset{K\ 6}{\rightleftarrows}} E *$ $D +* \underset{K-7}{\overset{K\ 7}{\rightleftarrows}} D *$ $M +* \underset{K-8}{\overset{K\ 8}{\rightleftarrows}} M *$ $G +* \underset{K-9}{\overset{K\ 9}{\rightleftarrows}} G *$

k or $K_i = k_i/k_{-i}$ are rate constants; * = surface site; [MeOH] = methanol concentration; [G] = glycerol concentration; [FFA] = free fatty acid concentration; [T] = triacylglycerol concentration; [E] = ester concentration; term for free fatty acid adsorption = $FFA + * \rightleftarrows FFA*$ where, k_8 and k_{-8} are rate constants for ER model and k_{10} and k_{-10} are rate constants for LHHW model.

The Hattori mechanism is similar to the LHHW mechanism, in this mechanism also if considers the adsorption of triacylglycerols on the surface of the catalyst as a limiting step of the process. the difference of these mechanisms is that in Hattori mechanism occur the formation of intermediate species from the reactions between the adsorbed methanol and the adsorbed tri, di and monoacylglycerols. Where, first, methanol is adsorbed, followed by triacylglycerol. At the respective catalytic sites, the triacylglycerol moves to the methanol containing site, leaving its site empty, thus forming an intermediate (methanol-triacylglycerol-active site). Soon after, this intermediate decomposes into diacylglycerol and methyl ester. The di, monoacylglycerol and glycerol adsorbed soon thereafter emerge from the surface of the catalyst to the volume.

The LHHW kinetic mechanism, where was considered adsorption of methanol as a limiting step of the conversion presents a best adjustment to the experimental data, in addition, presented less parameters. Thus, the adsorption of methanol as a first step is crucial for the reaction to occur and to obtain larger conversions. The parameters: the rate coefficient for adsorption of methanol (k_{MeOH}); the adsorption equilibrium coefficient of the total transesterification reaction (K_{eq}); and the adsorption equilibrium constant of methanol (K_M). The reaction constant values and other results and tables with the model equations can be found in the study by Kapil et al. (2011).

A hybrid material formed by the association of hydrotalcite and hydroxyapatite (HT-HAp) was studied by Brasil et al. [43] in the methylation reaction of soybean oil using the temperatures of 100, 180 and 240 °C in three different times (2, 4 and 6 hours) and methanol:oil molar proportions of 9:1, 12:1 and 15:1 in the presence of 5% by weight of HT-HAp. At the lower temperature, the authors did not observe conversions to methyl esters independently of the other variables and concluded that higher temperatures are required for higher conversions. The maximum yield obtained by the author was 80% at the temperature of 240 °C and the methanol:oil molar ratio of 12:1 for 4 hours of reaction.

The temperature, in this case, may be a limiting factor for transesterification reaction, requiring high temperatures to activate the catalyst, which may render the process unfeasible.

The hydrotalcites have basic properties, but their primitive form is not often used in catalysis because their catalytic sites do not have easy access (Cavani et al. 1991)[78]. Therefore, Benedicto et al. (2018)[41] studied the deposition of potassium salts on the surface of the catalyst as a way of improving the catalytic capacity of the MgAl hydrotalcite. The original synthesized material was called HTk and the rebuilt catalyst was called HTCRk, both catalysts were used for biodiesel synthesis under temperatures not exceeding 65 °C. With the simple hydrotalcite, after 20 hours of reaction no conversion was observed, but with the catalyst modified with K^+ (potassium) cation a conversion of more than 80% was observed after 3 hours of reaction. The reaction conditions are shown in Table 1. The increased catalytic activity is associated with increased distortion of the catalyst layers, improving accessibility to active sites.

3.4. Kinetic models

In this item, kinetic models used to describe the transesterification reactions using different heterogeneous catalysts will be discussed. In this review, only studies with conversion above 96.5% in ethyl or methyl esters were referenced, since in computational process simulation, reactions with high alkyl ester conversions normally meet the biodiesel specifications of regulatory agencies with lower costs.

Several kinetic models have been used to describe the reaction of transesterification catalyzed by heterogeneous catalysts, the pseudo-first-order and the pseudo-second-order models being more common and the more complex models based on the reaction mechanisms of ER and LHHW.

Prado et al. (2016)[58] studied soybean oil and macauba oil as the source of triacylglycerols, methanol and ethanol as solvents and Ca and Al mixed oxide as heterogeneous catalyst, obtained from the synthetic hydrocalumite (Ca-Al). Using soybean oil, they obtained a conversion to fatty acid methyl esters of 97 % after 1.5 h of reaction, and 91 % of conversion to fatty acid ethyl esters (FAEE) after 12 h of reaction. For macauba oil, 95 % FAME conversions were observed after 1.5h of reaction and 69 % FAEE conversion ester after 12 hours of reaction. The transesterifications were performed using a catalyst percentage of 3% in relation to the mass of oil, a molar ratio of alcohol:oil of 14:1, subjected to a temperature of 65 °C and stirring at 600 rpm.

Using these conditions, the authors modeled the reaction kinetics considering a pseudo-first-order model due to the great excess of ethanol or methanol in the reaction, according to the equation below

$$-\frac{d[TG]}{dt} = k[TG][ALCOHOL] \qquad \text{Eq. (1)}$$

where, -d[TG]/dt is the consumption of triacylglycerols (TG) per unit of time (t), k is the reaction rate constant, *[TG]* is the concentration in TG, [ALCOHOL] is the concentration of ethanol or methanol.

In the reaction, the author considers that in the catalytic surface only the alcohol adsorbs, because it is considered to follow the Eley-Rideal mechanism, according to Dang et al.(2013)[79]; an insignificant change in catalyst concentration was also considered; very low values in the concentrations of monoacylglycerols and diacylglycerols were assumed, considered, therefore, constant; and it was also adopted that the reaction occurs in a set of three steps and no reverse reaction was evaluated. After all the considerations, the author reduced the equation as described below.

$$-\frac{d[TG]}{dt} = k[TG]\theta_{alcohol} = k'[TG] \qquad \text{Eq. (2)}$$

where $\Theta_{alcohol}$ is adopted as being the degree of recovery of alcohol after being adsorbed at the catalytic sites and $k' = k\Theta_{alcohol} \approx constant$, because, according to the authors, this value can be considered constant when alcohol is used in excess.

Rearranging and integrating, the following equation was obtained:

$$\ln[TG] = \ln[TG]_0 - k't \qquad \text{Eq. (3)}$$

The graphs of ln[TG] versus time was plotted and k' is the slope of the regression line.

Prado et al. (2016)[58] determined kinetic data using soybean oil and macauba oil and ethanol and methanol as solvents. In their study, they observed much slower reaction rate when ethanol was used, with an apparent velocity constant (k') equal to 0.22 h^{-1} ($R^2 = 0.98$). For methanol, the constant found was 2.88 h^{-1} ($R^2 = 0.98$). The authors concluded that the reaction rate was higher for methanol due to its higher acidity (pKa = 15.5) in relation to ethanol (pKa = 15.9), which is lightly fewer acidic. Thus, they noted that methanol favors the transesterification reaction. In addition, the authors observed a slower reaction rate for macauba oil with a constants k' = 2.57 h^{-1} using methanol and k' = 0.13 h^{-1} when using ethanol. They attributed this behavior to a higher external diffusion resistance due to a higher viscosity of macauba oil caused by the higher amount of saturated compounds present.

Jamal et al. (2015)[48] in their research evaluated the reaction of transesterification of soybean oil with methanol and Amberlyst A26OH resin as heterogeneous catalyst with and without the presence of FFA. Two kinetic models of surface reaction (ER and LHHW) were used to explain the rate of methanolysis with and without the presence of FFA and help elucidate the reaction process that occurs on the surface of the catalyst. These reaction conditions are described in Table 1. These authors considered that the conversion rates of di and monoacylglycerols (the intermediates formed during the reaction) were much higher than the adsorption rate of methanol (the adsorption of methanol is the limiting step of reaction, because without the formation of methoxide the reaction will not begin) and therefore could be disregarded. These authors also observed by means of the reaction kinetics that the presence of the FFA favors the transesterification reaction promoting higher methanolysis rates. According to them, when the FFA approaches the basic surface of the catalyst, triacylglycerol, diacylglycerol and monoacylglycerols interact with the FFA by means of hydrophobic interactions and the hydrophilicity of the anion exchange resin is reduced. This interaction allows the acylglycerols to approach with greater ease of the basic surface, resulting in higher reaction rates. the simplified models can be seen in Table 3 and all the kinetic parameters can be found in the article of Jamal et al. (2015)[48] and the full version of the calculations can be found in the supplemental material of this study.

Table 3. Kinetic models used to adjust the experimental data.

Model	Rate equation, ($\frac{d[MeOH]}{dt}$ =)
ER kinetic model without FFA	$\frac{-k[MeOH]}{(1+K_7[G])}$
ER kinetic model with FFA	$\frac{-k[MeOH)}{(1+K_7[G]+K_8[FFA])}$
LHHW kinetic model without FFA	$\frac{-k[MeOH]}{(1+K_2[T]+K_6[E]+K_9[G])}$
LHHW kinetic model with FFA	$\frac{-k[MeOH]}{(1+K_2[T]+K_6[E]+K_9[G]+\ K_{10}[FFA])}$

Source: Adapted from Jamal et al. (2015)[48].

where [MeOH] = methanol consumed; k = constant of rate methanol consumption; K_7 e $K_9 = \frac{k_{forward}}{k_{reverse}}$ =constant of the reaction rate for glycerol; K_8 and K_{10} = rate constant for FFA adsorption; $K_{2=}$ rate constant for triacylglycerol adsorption; K_6= constant of the reaction rate for methyl ester; [G] = concentration of glycerol; [FFA] = concentration of FFA; [T] = concentration of triacylglycerol; and [E] = concentration of methyl ester.

Jamal et al. (2015)[48] evaluated the methanol consumption over the course of time for each model obtained. Using ER model, the methanol consumption rate constant was 7.48 x 10-4 h^{-1} without the presence of FFA and 1.94 h^{-1} with FFA present. For the LHHW model, the constant found for alcohol consumption was 6.20 x 10^{-2} h^{-1} without FFA and 1.71 h^{-1} with

FFA. Therefore, the author concluded that the FFA when present increases the rate for the consumption of methanol. The authors also concluded that the mechanism of reaction tends towards a hypothetical ER mechanism due to the methanol in excess used in the reaction. They further stated that the triacylglycerol concentration of the LHHW model provides a small influence in the denominator of the equation at excess level of methanol. But, as the molar ratio of methanol to triacylglycerol reduce, the importance of sorption of triacylglycerol in the resin increases, favoring the model. Thus, informed the reaction parameters, the models used point that methanol adsorption in the catalytic it's the crucial step in reactions where methanol is present in amounts above reaction stoichiometry.

Solis et al. (2017) [33] also performed kinetic studies using a catalyst that promoted the highest yield in biodiesel. Mayenite impregnated with 10% lithium (M2) was used to transesterify rapeseed oil. The molar ratio of methanol:oil was 6:1, with a percentage of catalyst of 5% with respect to the mass of oil, subjected to 60 °C and stirring of 180 rpm for 2 hours. These parameters were sufficient to reach the maximum yield in FAME conversion (100%).

Initially, to model the kinetics of reaction, Solis et al. (2017) [33] made a mass balance on a discontinuous reactor with agitation, according to the equation that follows.

$$V_{cat} r_A = \frac{dC_A}{dt} V_{tot} \rightarrow r_A = \frac{dC_A}{dt} \frac{V_{tot}}{V_{cat}} \qquad \text{Eq. (4)}$$

where, r_A is the reaction rate for triacylglycerol; C_A is the triacylglycerol concentration, t is the reaction time; V_{tot} is the total volume of the mixture inside the reactor; V_{cat} is the volume of catalyst and C_A is the triacylglycerol concentration at time t, and can be defined according to equation 5.

$$C_A = C_{A0}(1 - X_A) \qquad \text{Eq. (5)}$$

where C_{A0} is the triacylglycerol concentration in the time t=0 and X_A is the degree of conversion of triacylglycerol to alkyl esters.

Based on previous study, Solis et al. (2017) mentioned that the reaction of transesterification catalyzed by heterogeneous catalysts has three steps:

1) Initially, considering a three-phase system (methanol, catalyst and oil), the conversion

into fatty acid methyl esters may be low due to the mass transfer resistance which may increase the time for formation of the reactive phase of methoxide on the surface of the catalyst. These circumstances suggest a pseudo-second-order reaction rate;

2) In the second stage of the reaction, the production of biodiesel increases because the liquid mixture phase becomes more homogeneous and the methoxide formation occurs more quickly, now in a 2-phase reaction system (liquid-solid), causing an increase in the reaction rate. Thus, the reaction rate, according to the author, has been reported as being of pseudo-first-order;
3) And the third stage is represented by a decrease in the conversion rate due to the lower concentration of triacylglycerol.

Solis et al. [33] also cited that the overall equation of the transesterification reaction follows a fourth-order reaction rate. For displace the transesterification reaction to the formation of the product, methanol in excess was used. In this case, considering that the second step was predominant in the reaction (two-phase system), a kinetic model approximation of pseudo-first order was made. According to the equation below.

$$r_A = -kC_A C_B^3 \cong -k^* C_A \qquad \text{Eq. (6)}$$

where C_B is the concentration of excess methanol; k * is the pseudo-first order reaction constant.

Replacing, integrating and rearranging the equations for r_A and relating the variables of concentration, density and mass, we have to

$$\frac{d_{C_A}}{dt} = -k^* C_A \rightarrow \ln\left(\frac{C_A}{C_{A_0}}\right) = -k^* \left(\frac{V_{cat}}{V_{tot}}\right) t + C \rightarrow$$

$$\ln\left(\frac{C_A}{C_{A_0}}\right) = -k^* \left(\frac{\rho_{tot}}{\rho_{cat}}\right)\left(\frac{m_{cat}}{m_{tot}}\right) t + C \qquad \text{Eq. (7)}$$

The author has suggested a constant density ratio between total volume density and catalyst density which can be included in the apparent reaction rate constant as k^{**}, resulting in

$$-\ln(1-X_A) = k^{**}\left(\frac{m_{cat}}{m_{tot}}\right)t + C \qquad \text{Eq. (8)}$$

where, X_A is the mole fraction of triacylglycerol, m_{cat} is the mass of the catalyst and m_{tot} is the total mass.

To obtain the value of the apparent reaction constant, the author plotted a graph of -ln (1-XA) versus t, where k^{**} corresponds to the slope of the line. The value obtained for the apparent rate constant (k^{**}) was 0.0447 min^{-1} with an $R^2 = 0.97$, indicating an acceptable curve fit.

4. Discussion

As can be seen, optimum conditions for temperature, alcohol:oil molar ratio, catalyst concentration and stirring rate change for each type of catalyst to convert triacylglycerols into ethyl or methyl esters.

For the ion exchange resins, it was observed that the crosslinking density, porosity and degree of swelling of the catalyst have influence on the catalyst activity. Evaluating the results, the anion exchange resins showed to be more efficient for biodiesel production using low temperatures, which is a limitation for these materials because of their low thermal stability. However, in terms of the process, high conversion at mild temperatures is an important advantage that reduces costs and energy requirements and makes their use viable.

In the studies cited using anion exchange resins, no author took into account in the calculations of the molar ratio alcohol: oil the alcohol adsorbed in the resin during their conditioning. In addition to avoiding the unnecessary addition of alcohol, conditioning is beneficial because, according to Deboni et al. (2015)[80], alcohol causes a resin swelling effect. This effect promotes a reduction of the internal resistance to diffusion caused by the increase of the free path inside the resin, facilitating the diffusion of the solute to the active site.

As can be seen in Table 1, methanol was the alcohol most used in the reactions, first due to its low cost and second because it is more reactive when compared to ethanol, but it has the disadvantage of being toxic and water miscible, representing a danger to the environment [81] and from non renewable sources.

Another factor to note is that high conversions were obtained using high FFA oils such as cooking oils. Heterogeneous catalysts do not have sensitivity to FFA, once they are adsorbed by the heterogeneous catalyst and there is no soap formation, reducing the biodiesel purification steps [42,11,30,48,65].

It was also observed that faster reactions were obtained when using small amounts of catalyst. For the catalysts based on hydrotalcites, when high temperatures and high molar ratios were used, the conversions were not good enough for the studied conditions.

Mild temperatures were used by ion exchange resins, which is limited by their manufacturer's specification. The highest temperature used was 65° C for Amberlyst-A26 OH. Normally, times longer than 6 h were required to obtain high conversions.

For situations where high pressure and temperature conditions were used [55,44,43,59,60], high conversions were observed, which may also be due to the high molar ratio values used, except for the case of hydrotalcites.

5. Conclusion

Optimum conditions were shown for each type of heterogeneous catalyst, such as temperature, amount of catalyst, alcohol: oil molar ratio, stirring speed and reaction time. The reaction mechanisms of the catalysts were also presented and explained. Finally, it was possible to arrive at the conclusions that the adsorption of alcohol is the first step for the reaction of transesterification using heterogeneous catalysts, the anion exchange resins presented better performances for biodiesel production in relation to the other catalysts and for the calculation of the ratio molar of alcohol:oil the alcohol used in the pretreatment of the resin must be taken into consideration.

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CAPÍTULO 4

Optimization of the production of biodiesel from palm olein using strongly basic anionic resin as heterogeneous catalyst

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Optimization of the production of biodiesel from palm olein using strongly basic anionic resin as heterogeneous catalyst

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Abstract

Currently, due to the combat against climate changes and demand for renewable energy, biodiesel is likely to play an important role in fuel growth in the coming decades. By 2040, its share will be 8% in the road fuel demand. Studies involving the use of heterogeneous catalysts in biodiesel production have been highlighted due to the advantage that they can be easily separated for reuse and, thus, reduce product purification steps. In this study the performance of the Purolite A503S anion exchange resin as a heterogeneous catalyst in the transesterification reaction from palm olein for ethyl biodiesel production was investigated and the independent variables were optimized based on the maximum conversion in ethyl esters. For the optimization, the response surface methodology (RSM) coupled to a factorial design (2^3) with central composite rotatable design (CCRD) was used. The interactions of the effects of temperature, catalyst percentage and oil: ethanol molar ratio were evaluated. The reaction time of 10 hours was established relating conversion and reaction time and the stirring speed was determined by assessing the conversion potential ranging from 250-1000 rpm. The reactions were performed in a jacketed reactor coupled to a thermostatic bath and, at the end of the reactions, an aliquot was collected to quantify the triacylglycerols, diacylglycerols, monoacylglycerols, ethyl esters and ethanol by the HPSEC method and the glycerol was determined by stoichiometry. From the 17 factorial design trials, a predictive and significant second order model was adjusted to the results to explain the experimental data. From the optimized variables, a conversion of approximately 98 % in ethyl esters was obtained using 17.5% catalyst, oil: ethanol molar ratio 1:13 and temperature 50.1 ° C. Thus, in the studied conditions, despite the long reaction time, Purolite A503S resin presents itself as a potential heterogeneous catalyst for use in transesterification reactions.

Keywords: transesterification, ethyl ester, ethanol, fuel, Purolite resin, physical properties

1. Introduction

Palm olein is a product obtained through the fractionation of the refined palm oil. This operation consists of slow cooling and separation by filtration of the liquid phase (palm olein) from the solid one (palm stearin). Palm olein is liquid at lower temperature due to its rich composition in unsaturated triacylglycerols and can be used as an excellent source for biodiesel production for colder climate regions. Its composition has approximately 50 to 60 % of unsaturated fatty acids and raw materials with lower amounts of saturated fatty acids produce fatty acid ethyl esters (FAEE) or methyl esters (FAME) with lower turbidity point, because, high amounts of these components may cause clogging of vehicle engines due to crystal formation [1,3].

The biodiesel is generally produced by the transesterification reaction of a triacylglycerol present in vegetable oil or animal fat with a short chain alcohol, most commonly ethanol or methanol, to form fatty esters and glycerol. These reactions aim to reduce the viscosity of triacylglycerols, improving their physical properties for diesel engines [4,5,6,7].

In addition to the triacylglycerol source, the choice of alcohol is also very important for biodiesel production [1]. Methanol is the alcohol most used in biodiesel production reactions, due to its higher reactivity, low cost and availability [8,1]. However, since ethanol is non-toxic and can be obtained from renewable sources, it appears to be more appropriate, because with its use the biodiesel is obtained completely from renewable sources. [4,9,10]. In addition, the production of FAEE, rather than FAME, is of great importance, because it allows the production of a fuel with an extra carbon atom, which slightly increases the calorific value and cetane number of biodiesel and also has lower cloud point, improving engine starting in regions experiencing lower temperatures [11,8,9].

However, to accelerate the conversion rate to alkyl esters, the use of a homogeneous or heterogeneous catalyst is also required [6].

Homogeneous catalysts are most commonly used in transesterification reactions, however, they have some disadvantages, such as: the product separation and purification are more difficult; they cannot be reused; soap and water can be produced and large amounts of water are needed for purification [12,13]. Heterogeneous catalysts emerged to overcome these disadvantages as they can be considered more beneficial to the environment and industry as they have the ability to be regenerated and reused [14,15], non-corrosive [15], they can be applied in continuous processes and have easy separation of the obtained product [16].

Several heterogeneous catalysts have been studied in the literature and, recently, ion exchange resins have called attention because they have favorable reaction conditions, have the ability to transesterify and purify the product simultaneously and allow the use of operations under mild conditions [17,18]. Recently, several ion exchange resins have been used to investigate biodiesel production [20,21,18,22,23,24,25]. However, none studies involving the use of Purolite A503S resin as heterogeneous catalyst in transesterification reaction have been found in the literature.

The biodiesel production process can be affected by several factors depending on the reaction condition to be used. The main ones are: the type of catalyst and its concentration, the alcohol:oil molar ratio and the type of alcohol, the temperature and reaction time, and the mixing intensity or stirring speed of the reaction medium [4].

Optimizing these reaction parameters for biodiesel production using this type of catalyst consists of the main challenges found in the literature. Response surface methodology (RSM) has become a great alternative to achieve this goal[26]. This methodology consists of mathematical and statistical techniques extremely useful to evaluate the effects of independent variables in the process, allowing to determine the best operating conditions for biodiesel production [25,26]. Moreover, this technique allows to evaluate the interaction effects between variables, unlike conventional techniques, where the variables are analyzed one at a time, where the response becomes a function of a single variable. This analysis technique of one variable at a time is time consuming due to the large number of experiments and fails to demonstrate the parametric effects of the process.

Thus, the main factors affecting the transesterification reaction, reaction temperature, catalyst amount and palm olein: ethanol molar ratio, were investigated applying the response surface methodology assisted by a central composite rotatable design (CCRD).

2. Materials and methods

2.1 Materials

The palm olein was supplied by Agropalma S.A., located in Limeira (Brazil). The Purolite A503S resin used in the experiments as a heterogeneous catalyst was supplied by Purolite Brasil. This resin is classified as strongly basic and was chosen for the experiments because it has a good ion exchange capacity and a macroporous structure, which facilitates the penetration of alcohol and triacylglycerol molecules in the active sites of the resin. In addition, no studies involving this resin for biodiesel production have been found in the literature, and this further justifies its use. The characteristics of the Purolite A503S resin are presented in Table 1.

Table 1. Resin physical and chemical characteristics

Characteristics	Details
Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Functional Group	Type I Quaternary Ammonium
Commercialized Ionic Form	Cl^-
Total Capacity (min.), Cl^- form	1.0 eq/L
Particle Size Range	425-1200 µm
Temperature Limit, Cl^- Form	100 °C
Temperature Limit, OH^- Form	60 °C (OH^- form)

Source: Purolite Brazil

The solvents and reagents used in this work are described in Table 2 followed by the suppliers and the purity expressed as mass fraction.

Table 2. Solvents and reagents used in this study.

Component	Supplier	Country	Purity (% wt)
Ethanol	Merck	Germany	> 99.9
Sodium hydroxide	Dinâmica	Brazil	> 98
Mixture of partial DAG	SGS-GMG Agriculture and Industry ltd.	Brazil	52
Mixture of partial MAG	SGS-GMG Agriculture and Industry ltd.	Brazil	48
Toluene for HPLC	Sigma-Aldrich	EUA	> 99.9
Acetic Acid	Merck	Germany	100
Sodium Ethoxyde	Sigma-Aldrich	EUA	21

2.2 Methods

2.2.1 Resin Activation

Purolite A503S resin is marketed in Cl^- form according to the specifications shown in Table 1, for its activation it is necessary to replace the Cl^- ion by OH^-. The activation step was performed following the method described by the manufacturer. The resin was washed with deionized water until the liquid became clear. After washing, a 5 % NaOH aqueous solution in mass was percolated at a flow rate of 3 BV/h (bed volume/hour) for 2.5 hours. After this time, the resin was again subjected to the deionized water wash process to remove the excess NaOH and the NaCl formed during activation. The resin was purified using the same flow rate until the effluent pH reached the neutral value. After activation and purification, the water present in the resin was removed using anhydrous ethanol at the same flow rate used for activation for 2.5 hours. After removal of the water, the resin was stored immersed in ethanol so that the catalyst active sites do not react with CO_2 from the air and are deactivated [17]. For resin cleaning, as well as activation and purification, the resin was packed in a fixed bed column (63.0 cm long x 5.4 cm external diameter x 2.6 cm internal diameter) coupled to two peristaltic pumps, one for liquid feeding on the column top and the other for effluent removal on the column bottom, as shown in Fig. 1, both working at same flow rate. Activation and washing of the resin were performed at room temperature.

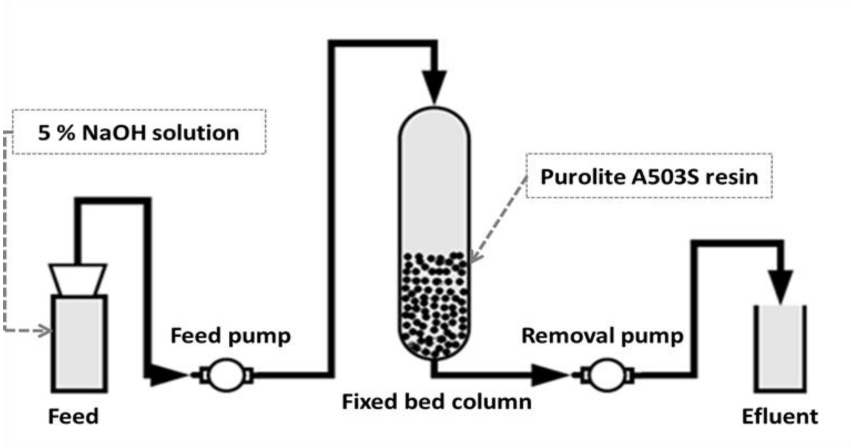

Fig. 1. Schematic drawing of the fixed bed column used for resin activation. Source: Author own, based on the manufacturer method.

2.2.2 Analysis of NMR of the Resin

The analysis of nuclear magnetic resonance (NMR) was performed with resins before activation (Cl- form) and after activation (OH- form). The samples were previously washed with ethanol and dried in a vacuum oven at 50 °C to constant weight.

The solid state NMR spectra of $^{13}C\{^{1}H\}$ of the resin were obtained on the Bruker AVANCE II + 400 MHz (9.40 T) spectrometer operating at a frequency of 100.6 MHz for ^{13}C. The combination of *Cross-Polarization Magic Angle Spinning* (CP/MAS) was used. To obtain the spectra, resin beads were accommodated inside a zirconia rotor (ZrO_2) using the following experimental conditions: spectral window of 278 to -17 ppm, 4.0 ms contact time, 2.0 s pulse interval, acquisition time 34 ms and sample rotation at 10 kHz.

2.2.3 Ethanol Retained in the Stored Resin

As aforementioned, the resin is stored immersed in ethanol and, therefore, ethanol is physically adsorbed to the resin. This amount of ethanol must be known and taken into account when calculating the total ethanol mass used in the experiments.

The percentage of ethanol retained in the activated resin was determined in a vacuum oven at 50 °C. The storage resin was drained, weighed in a Petri dish and kept in the vacuum oven until constant weight. The oven pressure was based on the vapor pressure of ethanol at 50 °C. The calculation for volatile quantification was made according to equation 1.

$$Ethanol\ in\ resin(\%) = 100 * \frac{m_{i-}m_f}{m_i} \qquad \text{Eq. (1)}$$

where m_i is the initial mass and m_f is the final mass.

2.2.4 Palm Olein Characterization

The free fatty acid (FFA) content , expressed in oleic acid, of the palm olein was determined using the official method IUPAC 2.201 (1987)[27] with the aid of an automatic titrator (Metrohm, 808 Titrando, Switzerland). Density of palm olein was determined in a densimeter (Anton Paar, model DMA 4500, Austria) at temperatures from 25 to 65 °C. Viscosity of palm olein were performed in temperatures from 25 to 65 °C using a stress-controlled rheometer (TA Instruments, AR1500ex, England) with stainless steel conical-plate geometry (diameter = 40 mm; range = 47 mm). The shear rate varied between 0 and 1000 s^{-1} and the flow curves were obtained in a sequential three flow steps: up-down-up cycles. The third flow curve data were fitted to the Newtonian fluid model using equation 3.

$$\sigma = \eta\gamma \qquad \text{Eq. (2)}$$

where σ is the shear stress (Pa), η is the viscosity (Pa s) and γ is the shear rate (s^{-1}).

The water content of palm olein was determined by Karl Fischer titration using an automatic Karl Fischer titrator (Metronm, 870 KF Titrino plus, Switzerland).

The oxidative stability index of the oil was determined in a Rancimat equipment (Metrohm, 893 Professional Biodiesel Rancimat, Switzerland) at 110 °C, 9 L/h of air flow rate, following the AOCS Cd 12b-92 official method (AOCS, 2009)[28]. The induction period (IP) was determined by the point of maximum inflection obtained from the second derivative of the conductivity curve, determined by the software of the equipment itself. All analyzes described in this topic were performed in triplicate.

2.2.5 Fatty Acid Composition

The fatty acid composition of palm olein was characterized and quantified by gas chromatography (Perkin Elmer, Clarus 600, USA) following the official method AOCS Ce 1f-96[28]. The equipment was equipped with FID (flame ionization detector) and a capillary column DB-WAX (Agilent Technologies, USA) with 30 m long, 25 mm internal diameter and 0.25 µm thick. Helium was used as a carrier gas at a flow rate of 1.78 mL/min, FID and injector temperature of 250 °C, 1 µL injection volume and column heating rate of 10 °C/min, starting at 50 °C and ending at 250 °C. Prior to injection, the samples were previously converted to fatty acid methyl esters (FAEE) following the methodology described by Hartman and Lago (1987)[29] adapted.

From the molar percentage in fatty acids of palm olein, the probable TAG composition was calculated using the algorithm described by Antoniosi Filho et al. (1995)[30]. The calculation is based on the combination of all fatty acids and results in a huge number of triacylglycerols and only TAGs with molar fraction greater than or equal to 0.5 % were considered. The probable composition in DAG and MAG was calculated from the composition in TAG, considering the probability of partial breakage of the TAG with no preference in breakage of the chemical bonds. These procedures were performed aiming to obtain the average molar mass of palm olein to be used in the calculation of the oil:ethanol molar ratio and to calculate the molar fractions of the components at the beginning and end of the reaction.

2.2.6 Chromatography for Fatty Components and Ethanol Characterization

For the quantification of fatty components (TAG, DAG, MAG and FAEE) and ethanol, the HPSEC chromatographic method was used according to the methodology described by Kittirattanapiboon and Krisnangkura (2008) and Aryee et al. (2011) [31,32], using a high performance liquid chromatograph (HPLC Shimadzu, model LC20AT, Japan) with automatic injector (Shimadzu, 20AT, Japan). Column oven temperature was 40 °C and injection volume 20 µL. As a mobile phase, a 0.25 % solution of acetic acid in toluene (v/v) was used at a flow rate of 1 mL/min, in isocratic mode, during 17 min of run.

The quantification of the components was made from five standard curves prepared with external standards of TAG, DAG, MAG, ethanol and purified ethyl biodiesel. The concentrations and area values of these five components were correlated by linear regressions, which were used for posterior quantifications. The ethyl biodiesel was obtained according to Silva et al. (2009)[33] from a homogeneous reaction using palm olein, sodium ethoxide (21 %) as catalyst, oil: ethanol molar ratio of 1:16, 60 °C temperature, 1 % catalyst in relation to mass of oil, subjected to agitation of 400 rpm for 30 min. After the reaction, the biodiesel was purified according to the methodology described by Silva et al. (2009)[33].

2.2.7 Transesterification Reaction

The transesterification reaction was performed using a jacketed batch reactor with a 50 mL volumetric capacity coupled to a digital thermostatic bath (Paar Physica, Viscotherm VT2, Germany) to ensure an isothermal process. The reactor was placed on a magnetic agitation plate (Ika, MAG HS 7, USA) with a cylindrical magnetic stirrer suspended in a metal support. The scheme shown in Fig. 2 exemplifies the apparatus. Initially, the resin, ethanol and palm olein were weighed in analytical balance (Precisa, XT220A). Subsequently, palm olein was heated until it reaches the reaction temperature. Simultaneously, the resin and ethanol were placed inside the reactor and stirred for 15 min until reaching the desired temperature. After this, palm olein was added to the mixture (ethanol + resin) and the reaction time was started to count.

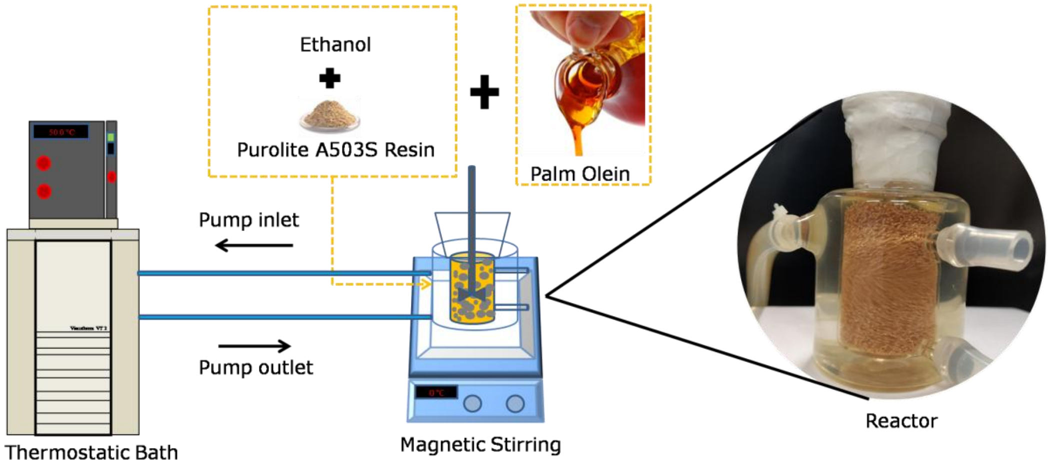

Fig. 2. Schematic drawing of the apparatus used in the transesterification reaction. Source: Author.

At the end of the reaction, approximately 100 µL of the mixture was collected and diluted in 5 mL of toluene and filtered using Nylon filters (25 mm diameter, pore 0.22 µm). After that, the content was injected in the HPLC to quantify the compounds, as described in item 2.2.6.The glycerol was determined by stoichiometry according described by Alva et al. (2020) [34].

The percentage conversion of palm olein to ethyl esters was calculated by the equation 3 below.

$$conversion(\%) = \left[1 - \frac{(3*N_{TAG,f}+2*N_{DAG,f}+1*N_{MAG,f})}{(3*N_{TAG,i}+2*N_{DAG,i}+1*N_{MAG,i})}\right] * 100 \qquad \text{Eq. (3)}$$

where, $N_{TAG,i}$, $N_{DAG,i}$, $N_{MAG,i}$, are the initial moles of tri, di and monoacylglycerols, respectively, and, $N_{TAG,f}$, $N_{DAG,f}$, $N_{MAG,f}$, are the final moles of tri, di and monoacylglycerols, respectively.

2.2.8 Relation between conversion and reaction time

Initially, previous tests were performed to define the conditions to be used in the conversion analysis with the reaction time. For this experiment, the temperature was fixed at 56.7 °C, 15.0 % of catalyst in relation to palm olein mass (g dry resin/100 g palm olein), oil:alcohol molar ratio of 1:13 and stirring speed of 400 rpm. Samples were collected every hour for 10 h to quantify TAG, DAG, MAG, FAEE and ethanol by HPSEC ang glycerol by stoichiometry. From 10 h the collection interval increased to 2 h up to 16 hours. The last point was collected in 24 h. These results are useful to fix the reaction time to be used in the experimental design.

2.2.9 Determination of Stirring Speed

To determine the stirring speed, the independent variables temperature, catalyst percentage and palm olein:ethanol molar ratio were fixed in the lower level of the experimental design described in item 2.2.10, 38.56 °C, 12.5 % and 1:10, respectively. The reaction time was determined according to item 2.2.8. The percentage conversion to FAEE was evaluated using 250, 400, 800 and 1000 rpm. The experiments took place as follows, when the reaction time has been reached, an aliquot was collected for HPSEC analysis for conversion calculation. Besides conversion to ethyl esters, the resin stress was analyzed during 5 reaction cycles. This analysis was performed by scanning electron microscopy (SEM) using a FEI/THERMO INSPECT F50 microscope in high vacuum mode ($<1.3\times10^{-2}$ Pa) installed at the Nanotechnology National Laboratory (LNNano, Campinas, Brazil)) belonging to the National Center of Research Energy and Materials (CNPEM). The samples were initially washed with absolute ethanol (99.5 %) to remove fatty components and glycerol and dried in a vacuum oven (Marconi, MA030/12, Brazil) at 50 °C to constant weight to remove volatiles. Due to the resin not being a good electrical conductor, making it difficult or impossible to obtain images, the samples were fixed in carbon tape stubs and covered with gold film to circumvent this problem, using the BAL-TEC equipment (SCD 050, Sputter). Resin morphology images were obtained by applying 200X magnifications and 2 kV beam voltage. From the SEM, particle size was also determined using the scales provided by the equipment.

2.2.10 Experimental Design

The experimental design evaluated the effects and interactions of the effects of temperature, catalyst percentage and oil:ethanol molar ratio on the percentage of conversion to ethyl esters. The proposed factorial planning was the central composite rotatable design (CCRD) with 2 levels and 3 factors (factorial design 2^3), 6 axial points and 3 repetitions at the central point, to determine the variability of results and evaluate the experimental errors, totaling 17 experiments, as shown in Tables 3 and 4. This type of planning was chosen for reducing the number of experiments and makes a study using a larger area of investigation. In addition, the order of the experiments was drawn, because, the randomization of the experiments avoids statistical distortions in the results [35].

Table 3. Levels and factors/independent variables of a planning $2^3$with points central and axial

Factors	Levels				
	-1.68	**-1**	**0**	**+1**	**+1.68**
Temperature (°C)	33.1	38.5	46.5	54.5	60.0
Catalyst (g dry resin/g palm olein)	10.8	12.5	15.0	17.5	19.2
Oil:ethanol molar ratio	1:7.96	1:10	1:13	1:16	1:18.04

Table 4. Factorial design with central composite rotatable design.

Experiments	Order[b]	Temperature (°C)	Catalyst (%)	Oil:ethanol molar ratio
1	3°	-1(38.5)	-1(12.5)	-1(1:10)
2	14°	+1(54.5)	-1(12.5)	-1(1:10)
3	12°	-1(38.5)	+1(17.5)	-1(1:10)
4	17°	+1(54.5)	+1(17.5)	-1(1:10)
5	15°	-1(38.5)	-1(12.5)	+1(1:16)
6	13°	+1(54.5)	-1(12.5)	+1(1:16)
7	9°	-1(38.5)	+1(17.5)	+1(1:16)
8	2°	+1(54.5)	+1(17.5)	+1(1:16)
9	8°	-1,68(33.1)	0(15)	0(1:13)
10	7°	+1,68(60)	0(15)	0(1:13)
11	16°	0(46.5)	-1,68(10.8)	0(1:13)
12	1°	0(46.5)	+1,68(19.2)	0(1:13)
13	6°	0(46.5)	0(15)	-1,68(7.96)
14	4°	0(46.5)	0(15)	+1,68(1:18.04)
15 (CP[a])	5°	0(46.5)	0(15)	0(1:13)
16 (CP)	11°	0(46.5)	0(15)	0(1:13)
17 (CP)	10°	0(46.5)	0(15)	0(1:13)

CP[a] = central point; Order[b] = order in which the experiments were performed

From the results obtained and the coded variables of Table 4, a second order polynomial model was generated to obtain the predicted values and calculate of the relative errors. The data were then evaluated by analysis of variance (ANOVA) and the significance of regression and lack of fit model were assessed by F-test. The quality of the fit of the second order equation was evaluated by the determination coefficient R^2. After verifying the quality of the model to describe the experimental data, response surfaces and contour curves were generated using Statistica 8.0 Software. Model validation experiments were performed at a point where the independent variables were not part of the experimental design and were within from studied region. For validation, the point of maximum conversion in FAEE was chosen.

For the transesterification reaction, time and agitation were fixed as described in items 2.2.8 and 2.2.9, respectively. The time was fixed because it is a variable that will always have a significant effect on the responses (either for the conversion reaction in FAEE or even cause an inverse reaction), and this characteristic may cause a decrease in the effects of other variables where there is a greater interest in studying. Also, the stirring speed was fixed, aiming to disregard the external resistance to mass transfer and from the moment that this resistance becomes negligible, it is believed that the effect of this variable will become insignificant on the results.

3. Results and Discussion

In this topic the results are presented and discussed.

3.1 Physical and Physicochemical Properties of Palm Olein

Initially, palm olein presented a percentage of free fatty acids (FFA) expressed as oleic acid of 0.05 %, below the maximum required by *Cordex Alimentarius* for refined oils [36]. This analysis served to give the information on oil quality, and for biodiesel production using anion exchange resin was a very useful parameter, since, the presence of FFA in large quantities can disable the catalytic sites of the resin, reducing the conversion into FAEE [17]. And, evaluate the effect of FFA presence on biodiesel production is beyond the scope of this paper.

For the viscosity and density values, it was observed that both properties decreased with increasing temperature (Table 5). The viscosity and density values were similar to that determined by Abdolmalek et al. (2019)[37] who, in their study evaluating the physicochemical properties of oils, determined for palm olein the density at 25 °C of 0.891 g/cm^3 and viscosity of 0.069 Pa.s [37]. The difference between the results is likely to be attributed to the climatic and soil differences of the regions from which palm fruits were harvested. Comparing the viscosity of palm olein with that of other oilseeds, it was observed that at 35 ºC the olein has a viscosity higher than that of other oilseeds such as canola and olive oils (42.48 mPa.s and 46.29 mPa.s, respectively) [38]. This is because, these two sources of triacylglycerols have in their composition a greater amount of unsaturated fatty acids [39,40] and, the increase in double bond causes a reduction in viscosity[41].

Table 5. Viscosity and density of the palm oil

Temperature (°C)	Density (g/cm³)	Dynamic Viscosity (Pa.s)
25	0.90922	0.076±0.004
35	0.90228	0.0531±0.0004
45	0.89542	0.034±0.0
55	0.88862	0.0312±0.0002
65	0.88191	0.0243±0.0003

In relation to the water content, palm olein presented 0.06 % ± 0.006. According to Sani et al. (2014)[11], water promotes hydrolysis of triacylglycerols, producing FFA and diacylglycerol. For alkaline catalysis reactions, raw materials with water concentrations of less than 0.06 % in mass of oil are required to produce no more free fatty acids [42,43]. In the literature, the resin resistance to water has also been studied. Ren et al. (2012)[44], using the anionic resin D261 with quaternary ammonium functional group, observed that the conversion to methyl esters decreased from 95.2 % to 87.7 % with water content increasing from 0.0 % to 1.0 % by mass. According to the authors, water can disable OH^- catalytic active sites because water molecules bind more effectively to the active sites than methanol.

Paterson et al. (2013)[45], evaluating Amberlyst 15 resin (Alfa Aesar Co., Ward Hill, USA) and adding percentages of water in the feedstock by up to 1.0 % in mass, did not observe effects on reaction products measured by HPLC (with 0.1 %, 0.5 % and 1.0 % were obtained conversions of 95.8 %, 95.2 % and 96.3 %, respectively). With 2.0 % water per oil mass, a decreased conversion to products (92.6 % conversion) was able to observe. In addition, the presence of water may decrease oil solubility in ethanol[46], and may possibly lead to a reduction in the conversion rate. Thus, this information leads to the conclusion that water content found in palm olein will not affect the conversion percentage.

The induction period (IP) defines the expected useful life of vegetable oils and fats and it is a parameter that depends on the number and position of the double bonds [47–49]. Although palm olein has a high content of unsaturated fatty acids, its induction period was 50 h, similar to that found by Pereira et al.(2019) [49] for bacuri fat, which in their work found a IP of 49.6 h determined at 130 °C and air flow at 20 L/h.

3.2 Fatty Acid Composition

Table 6 shows the fatty acid composition of palm olein (expressed as a percentage of total fatty acids). The values were also within or very close to the values determined by *Codex Alimentarius*[50]. It can be observed that palm olein presents mainly in its composition unsaturated fatty acids (oleic and linoleic acid). However, approximately 37 % of palmitic acid can still be found. These results are in agreement with the literature [1,3]. These features are useful for biodiesel production in regions that experience lower temperatures, since, raw materials with higher concentrations of unsaturated fatty acids can produce lower turbidity biofuels which reduce crystal formation and prevent engine clogging due to these crystals [2].

Table 7 express the likely TAG and DAG compositions present in palm olein. From the molar masses of each TAG and DAG and their respective molar fractions, the average molar masses of each fatty class were calculated. Table 8 shows the results of TAG and DAG concentrations of the palm olein, measured in HPSEC chromatographic method. The results were used to calculate the average molar mass of palm olein, which presented a value of 828.49 g/mol. The MAG content in the raw material was negligible because was below the limit of quantification.

Table 6. Fatty acid composition of the palm olein

Fatty acid	Symbol	C *x:y*[a]	W*100[b]	SD[C]
Dodecanoic	L	12:0	0.56	0.03
Tetradecanoic	M	14:0	1.02	0.01
n-Hexadecanoic	P	16:0	37.02	0.05
Octadecanoic	S	18:0	4.16	0.03
9-Octadecenoic	O	18:1	47.19	0.07
cis-9,cis-12-Octadecadienoic	Li	18:2	9.72	0.06
Eicosanoic	A	20:0	0.37	0.01

[a] C *x:y*, where, *x* = number of carbon and *y* = number of double bond; [b] W = mass fraction; SD = standard deviation

Table 7. Probable triacylglycerol and diacylglycerol composition of the palm olein

TAG	C *x:y*[a]	MM[b] (g/gmol)	X[c]*100	MM*X	DAG	C *x:y*[a]	MM (g/gmol)	X*100	MM*X
PPM	46:0	779.28	0.56	4.36	**OO**	36:2	620.99	23.00	142.83
LOP	46:1	777.26	0.94	7.31	**OLi**	36:3	618.97	8.47	52.43
PPP	48:0	807.33	5.47	44.16	**PO**	34:1	594.95	39.70	236.20
MOP	48:1	805.32	1.56	12.56	**SO**	36:1	623.00	1.92	11.96
OOL	48:2	803.3	0.85	6.83	**PLi**	34:2	592.93	8.44	50.04
POP	50:1	833.37	23.86	198.84	**AO**	38:1	651.06	0.20	1.30
PLiP	50:2	831.35	5.78	48.05	**LiLi**	36:4	616.95	0.79	4.87
OOP	52:2	859.41	27.94	240.12	**LP**	28:0	512.81	0.32	1.64
PLiO	52:3	857.39	11.18	95.86	**LO**	30:1	538.84	0.89	4.80
LiLiP	52:4	855.38	1.16	9.92	**MP**	30:0	540.86	0.38	2.06
POA	54:1	889.48	0.58	5.16	**PP**	32:0	568.91	15.70	89.32
OOS	54:2	887.46	2.85	25.29	**PA**	36:0	625.02	0.20	1.25
OOO	54:3	885.44	10.28	91.02					
OOLi	54:4	883.43	5.81	51.33					
LiLiO	54:5	881.41	1.18	10.40					
			MM_{TAG}	**851.22**				**MM_{DAG}**	**598.69**

[a] C *x:y*, where, *x* = number of carbon and *y* = number of double bond; [b] MM = molar mass; X[C] = molar fraction

Table 8. Acylglycerol composition of the palm olein

Acylglycerol	MM[a] (g/gmol)	W[b]	X[c]	MM palm olein
TAG	851.22	0.93	0.91	828.49
DAG	598.69	0.07	0.09	

[a] MM = molar mass; W[b] = mass fraction; X[c] = molar fraction

3.3 Catalyst characterization

Initially, Purolite A503S resin showed a percentage of valatiles of 74.0 %. The Fig. 3 shows the NMR spectra of the Purolite A503S resin before activation (A) and after activation (B).

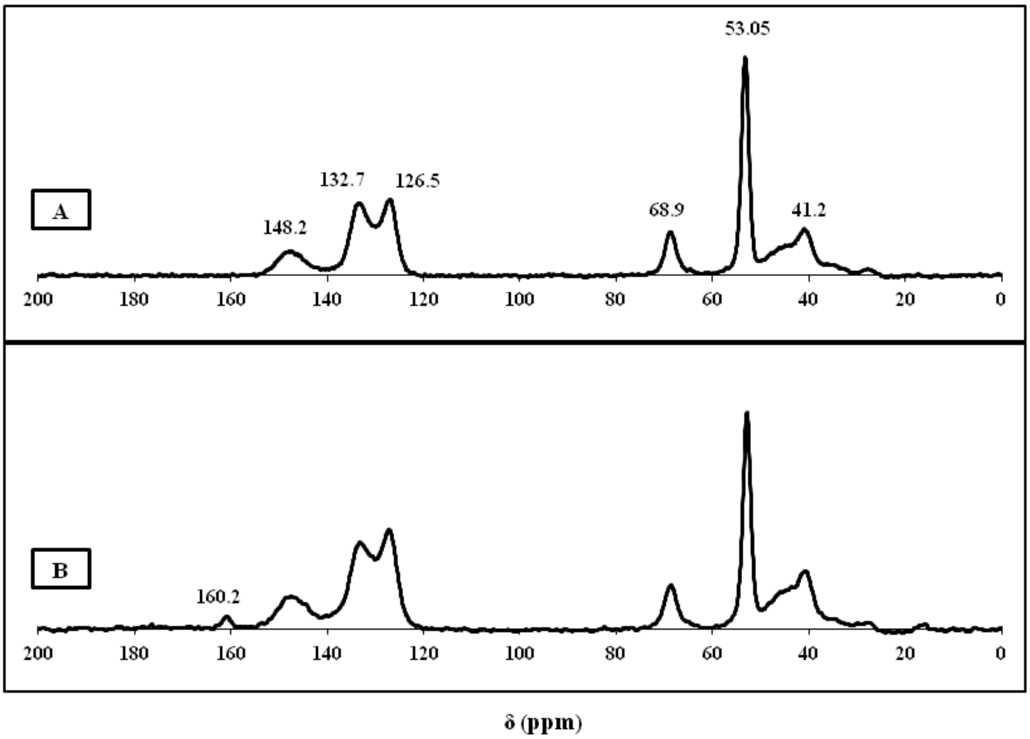

Fig. 3. NMR spectra $^{13}C\{^{1}H\}$CP/MAS obtained from Purolite A503S resin before activation (A) and after activation (B).

In the figure of the non-activated resin (Fig. 3A) it is possible to notice the signals between 41.2 and 68.9 ppm that may related to the aliphatic carbons of the resin structure and the region between 126.5 and 148.2 ppm correspond to the aromatic carbons also contained in the structure of the catalyst [17].

In the figure containing the activated resin (Fig. 3B), the 160.2 ppm signal observed in this spectrum is related to the species HCO_3^- (hydrogen carbonate), which can be formed from the reaction of hydroxyl (OH^-) present in the resin with atmospheric CO_2 (carbon dioxide) [17] As the resin was dried for analysis, its active sites were free, thus allowing, the adsorption of CO_2.

3.4 Influence of the Time in the Transesterification Reaction

Fig. 4 presents the conversion percentage in relation to the reaction time. It can be noted that in the first hour of reaction a conversion greater than 50 % in ethyl esters had already been obtained, in the first 4 hours the conversion exceeded 80 %. From the curve, it can be observed three behavior profiles of the transesterification reaction: A steeper curve in the first 4 hours of reaction; from 4 up until 10 hours there is already a decrease in the conversion rate; and after 10 hours, the reaction takes place very slowly. The choice of time was based where the reaction speed starting to become very slow, i.e., in 10 hours.

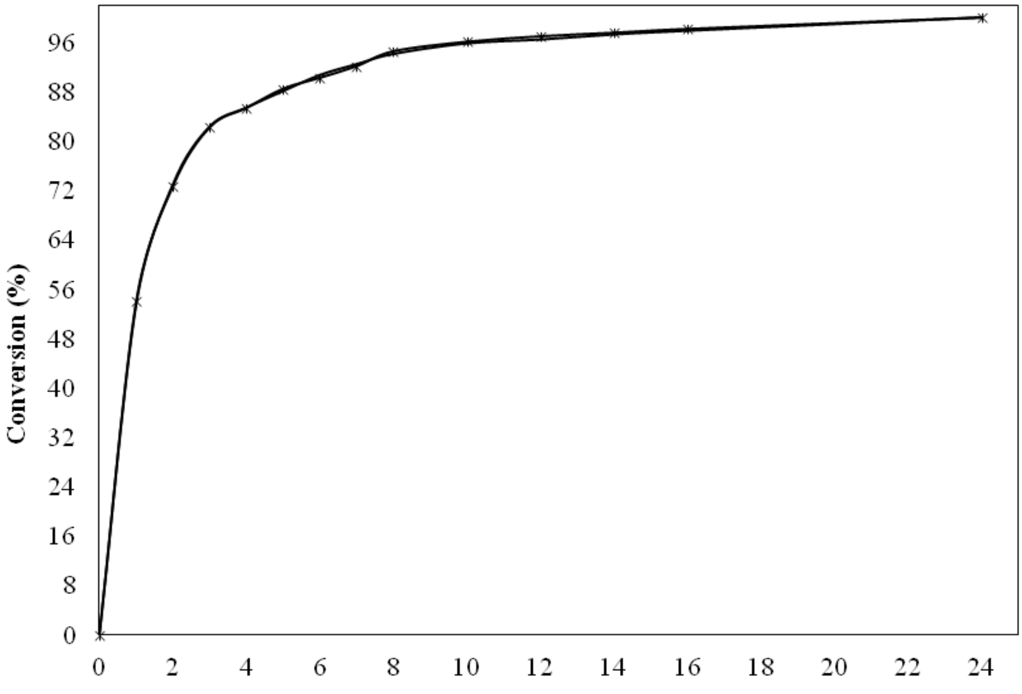

Fig. 4. Transesterification reaction profile over time using 15.0 % catalyst, oil:ethanol molar ratio of 1:13, temperature of 56.7 °C and stirring of 400 rpm.

3.5 Influence of the Stirring Speed

Table 9 shows the results of the effect of stirring on external resistance to mass transfer. The stirring speed was varied from 250 to 1000 rpm. In this study, at the end of the 4 experiments at 38.56 °C, 12.5 % catalyst, oil:ethanol molar ratio of 1:10 and 10 hours of reaction time, an aliquot was collected to quantify the fatty components on HPSEC analysis and determine the conversion in FAEE. The experiments were conducted up to 50 hours and the effect of agitation on resin morphology was evaluated, as shown in Fig. 6, in the images obtained by SEM.

Table 9. Effect of stirring on TAG to FAEE conversion

Stirring (rpm)	**250**	**400**	**800**	**1000**
FAEE Conversion (%)	73.7	72.9	72.7	75.0

Evaluating the effect of this variable on the conversion to FAEE, differences between the values can be observed, however, there is no linearity in the responses, which leads to the conclusion that 250 rpm agitation was sufficient to eliminate the effect of external resistance to mass transfer, since the differences between the results can be attributed to random errors. However, due to observations made during the experiments, 400 rpm agitation was chosen to continue the study, because it was observed that the particles distributed more evenly in the reactor (Fig. 5A), and the agitation that ensures the homogeneity of the medium is ideal for reactions. At 250 rpm, part of the particles stayed deposited in the bottom of the reactor (Fig. 5B).

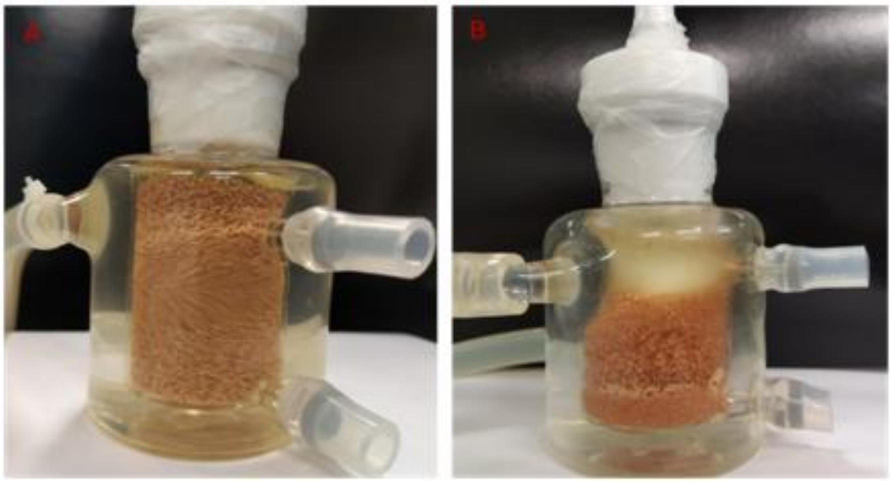

Fig. 5. Reactions submitted to agitation at 400 rpm (A) and 250 rpm (B). Source: Author.

It can be seen from the images that Purolite A503S resin has a spherical shape with different particle sizes, i.e., a very heterogeneous diameter range. In these images, a minimum diameter of 470.6 µm (Fig. 6A) and a maximum diameter of 968.1 µm (Fig. 6B) were observed. In the manufacturer specification for the resin (Table 1) the stipulated size range was 425-1200 µm. In the study of Shibasaki-Kitakawa (2007)[53] the average particle size range for the anionic resins Diaion PA306 and Diaion PA306S (Mitsubishi Chemical Corporation, Japan) were 400-600 µm and 150-250 µm. A smaller range compared to Purolite A503S resin. This information was important for this study, because at the time of weighing, the resin was severely homogenized in order to minimize the experimental errors due to particle size distribution.

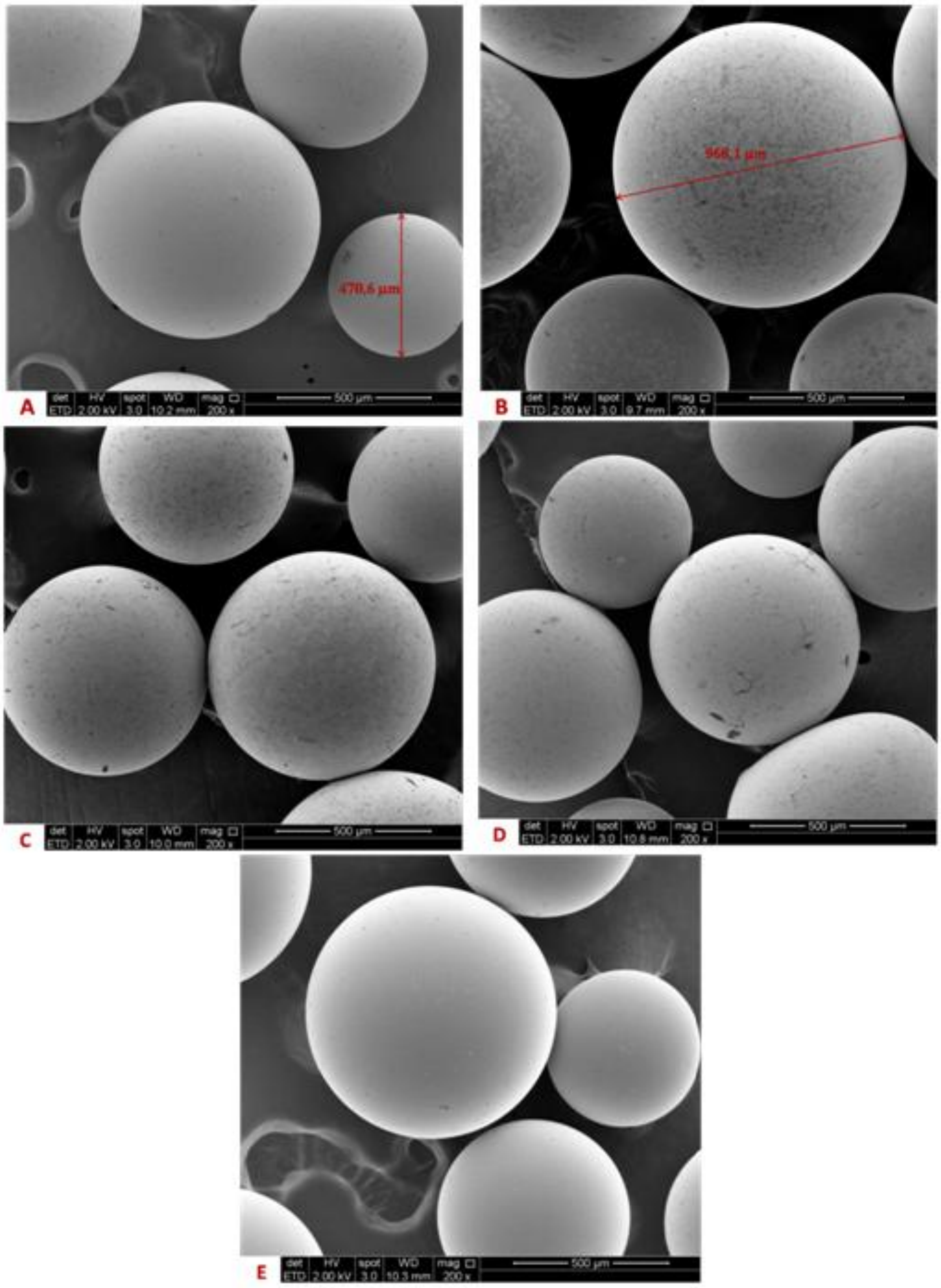

Fig. 6. Scanning Electron Microscopy from Purolite A503S Resin Before Reaction (A) and after 50 hours of agitation submitted to 250 rpm (B), 400 rpm (C), 800 rpm(C) and 1000 rpm (D).

Observing the morphology of the resin in the control sample (Fig. 6A), it was noted a slick aspect, without fissures. The samples submitted to different stirring speeds during 50 h did not differ much from the control sample. They feature only small scratches, probably coming from resin-resin shear and/or resin-reactor shear, and small stains that may be due to the presence of ethyl esters on the catalyst surface. Thus, from the images obtained by SEM, it was observed in this study that the stirring speed did not cause a greater catalyst wear.

3.6 Optimization of the Ethyl Ester Production Using RSM

The FAEE conversion results obtained from the experimental design, using the independent variables catalyst (%), temperature (°C) and oil:ethanol molar ratio, are shown in Table 10. From the coded matrix and the experimental results, the coefficients of the second order regression model were obtained, as shown in equation 4.

$$\text{Conversion (\%)} = 96.31 + 2{,}51{*}MR + 4.47{*}C + 2.94{*}T - 2.86 * MR^2 - 1.79{*}C^2 - 1.04{*}T^2 - 2.39{*}MR{*}C - 0.91 * MR{*} T - 2.12{*}C{*}T \qquad \text{Eq. (4)}$$

where MR is the molar ratio, C is the catalyst percentage, T is the temperature, MR^2, C^2 and T^2 are the quadratic variables and MR*C, MR*T and C*T represent the interactions between the variables.

From the model, the predicted values and their respective absolute deviation and relative deviation could be calculated, as shown in Table 10. It can be observed that the relative errors between the observed values and the predicted ones were low, evidencing a good fit of the model to the experimental data. From the analysis of variance (ANOVA) shown in Table 11, it was found that, with a significance of 5 % ($\alpha = 0.05$) the Fcalc for the regression (13.34) was higher than the Ftab, showing that the regression is significant and from Fcalc to the lack of fit (2.30), that was lower than Ftab, it was found that the lack of fit was not significant, i.e., the model fits the experimental data. In addition, the percentage of variation explained (R^2) was very good, presenting a coefficient of determination of 94.5 %. Thus, it can be concluded that the model is useful and predictive to explain the experimental data; and, in this way, it can be used to generate the response surfaces and contour curves to optimize the variables.

Table 10. Experimental conversion values, predicted by the model and deviations for CCRD

Test	Variables			Observed (%)	Predicted (%)	Absolute deviation	Relative deviation (%)
	MR[a]	Catalyst (%)	Temperature (°C)				
1	-1 (1:10)	-1 (12.5)	-1 (38.56)	72.9	75.22	2.34	3.20
2	-1 (1:10)	-1 (12.5)	1 (54.56)	87.7	87.2	0.50	0.60
3	-1 (1:10)	1 (17.5)	-1 (38.56)	94.64	93.23	1.42	1.50
4	-1 (1:10)	1 (17.5)	1 (54.56)	97.59	96.71	0.90	0.90
5	1 (1:16)	-1 (12.5)	-1 (38.56)	85.9	86.89	1.00	1.20
6	1 (1:16)	-1 (125)	1 (54.56)	93.68	95.2	1.53	1.63
7	1 (1:16)	1 (17.5)	-1 (38.56)	94.7	95.31	0.60	0.64
8	1 (1:16)	1 (17.5)	1 (54.56)	97.34	95.11	2.23	2.30
9	-1.68 (1:7.96)	0 (15)	0 (46.56)	83.63	83.96	0.33	0.40
10	1.68 (1:18.04)	0 (15)	0 (46.56)	92.92	92.43	0.50	0.50
11	0 (1:13)	-1.68 (10.8)	0 (46.56)	86.24	83.7	2.54	2.90
12	0 (1:13)	1.68 (19.2)	0 (46.56)	96.38	98.76	2.40	2.50
13	0 (1:13)	0 (15)	-1.68 (33.12)	89.87	88.42	1.45	1.61
14	0 (1:13)	0 (15)	1.68 (60)	97.04	98.33	1.30	1.33
15 ©	0 (1:13)	0 (15)	0 (46.56)	94.35	96.31	2.00	2.10
16 ©	0 (1:13)	0 (15)	0 (46.56)	97.47	96.31	1.20	1.20
17 ©	0 (1:13)	0 (15)	0 (46.56)	97.08	96.31	0.80	0.80

MR[a] = Molar Ratio (oil:ethanol)

Table 11. Lack of fit test and regression analysis for the generated second order model

Variation source	[b]QS	[c]SD	[d]QM	[e]$F_{CALC.}$	[f]$F_{TAB.}$
Regression	672.11	9.00	74.68	13.34	$F_{9; 7; 0.05}=3.68$
Resídual	39.19	7.00	5.60		
Lack of fit	33.38	5.00	6.68	2.30	$F_{5; 2; 0.05}=19.30$
Pure error	5.80	2.00	2.90		
Total	711.29	16.00			
[a]R^2 (%)	94.5				

[a]R^2 = % variation explained; [b]QS = Quadratic Sum; [c]SD = Standard deviation; [d]QM = Quadratic mean; [e]$F_{CALC.}$ = F value calculated; [f]$F_{TAB.}$= F value tabulated

Table 12 shows the statistical parameters of the t-test, F-test, and p-value used to verify and confirm the significance of the factors studied. The t-value measured how large the regression coefficient was in relation to its standard error and was obtained by dividing each coefficient by its standard error. A small p-value suggests that the coefficient is a large signal compared to noise because it is very large to arise by chance [54].

Table 12. Statistical significance of the variables. (L) Represents the linear terms, (Q) the quadratic terms and 1L by 2L, 2L by 3L and 1L by 3L terms referring to the interactions between the variables.

Factor	**[a]Regr. Coeff.**	**Pure Error**	**[b]t(2)**	**[c]p**	**-95% [d]Cnf. Limt**	**+95% Cnf. Limt**
Mean	96,31	0.98	98.11	0.0001	92.10	100.50
(1)Molar Ratio(L)	2,52	0.46	5.46	0.0320	0.54	4.50
Molar Ratio(Q)	-2.87	0.51	-5.65	0.0300	-5.05	-0.70
(2)Catalyst(%)(L)	4.48	0.46	9.72	0.0100	2.51	6.46
Catalyst(%)(Q)	-1.80	0.51	-3.54	0.0710	-3.98	0.39
(3)Temperature(ºC)(L)	2.95	0.46	6.39	0.0240	0.96	4.93
Temperature(Q)	-1.04	0.51	-2.04	0.1800	-3.22	1.14
1L by 2L	-2.40	0.60	-3.98	0.0580	-4.99	0.19
1L by 3L	-0.92	0.60	-1.52	0.2700	-3.51	1.67
2L by 3L	-2.12	0.60	-3.53	0.0720	-4.72	0.47

[a]Regr. Coeff. = regression coefficients; [b]t(2) = t-test or student t-test used to verify the contribution of the variable in the regression; [c]p = p-value used to verify the significance of variables; [d]Cnf.Limt = confidence limit.

Thus, factors with p-value < 0.05 were considered statistically significant at a confidence level of 95 %. Another way of check significance is through the 95 % confidence interval, where for effects to be considered significant the range must not include zero [35]. In this way, the linear term of catalyst (%), temperature and oil:ethanol molar ratio and the quadratic term of oil:ethanol molar ratio were considered statistically significant, because they presented a p-value < 0.05 confirming their effects on the responses. Small p-values are associated with a higher value of t, and the t-value is also useful for measuring the strength of the variable, because the higher the t-value, greater the effect of the variable on the response [54]. Therefore, for the levels studied, the variable that had the greatest effect on the response was catalyst (%), followed by the linear temperature term.

Usually, it is common in the literature to perform the reparametrization of the model, which consists in removing non-significant variables and recalculate the ANOVA [55]. However, in this study, the non-significant regression variables were not removed in order to avoid reduce the quality of the model, because, some variables were very close to be significant, and, the main objective of the model was to assist in optimizing the variables by maximum conversion to ethyl esters and not, in process control.

Analyzing the Fig. 7, it can be seen that the optimum region for temperature was between 46.56 °C and 54.56 °C, for the amount of catalyst and oil:ethanol molar ratio the optimum region was around 17.5 % of catalyst and oil: ethanol molar ratio 1:13.

The variables were optimized by the maximum conversion to ethyl esters and this point was also used for model validation. Table 13 shows the results of the point of maximum FAEE conversion predicted by the model and that obtained experimentally using a catalyst percentage of 17.5 %, temperature 50.1 °C and oil:ethanol molar ratio of 1:13.

Table 13. Model optimization and validation at point maximum conversion (17.5 % catalyst, temperature 50.1 °C and oil: ethanol molar ratio 1:13).

Response Variable	**Results**		**Relative Deviation**	**RMD***
	Predicted	**Observed**		
Conversion (%)	99.15	98.00	1.17	1.35

* Relative mean deviation

It can be observed that, although there is a difference between the predicted and observed values (99.15 % and 98 %, respectively), the validation experiment was quite satisfactory, because, the values are very close and the relative deviation for these two observations (1.17) was less than the relative mean deviation (1.35) obtained from the arithmetic mean of the 17 trials of the Table 12.

Results found by Deboni et al. (2018) [17] resemble those found in this paper. These authors used soybean oil, ethanol and the Amberlyst-A26 OH anion exchange resin and achieved a conversion greater than 99 % with a soybean oil:ethanol molar ratio of 1:16, 20 % catalyst on dry basis by mass of oil, 50 °C temperature and stirring at 500 rpm for 6 hours of reaction.

3.7 Variables Effect on Transesterification Reaction

It can be seen in Fig. 7A and 7C that a decrease in catalyst concentration causes a reduction in conversion to ethyl esters,, probably caused by a lower availability of active sites to react with ethanol molecule and form the ethoxide that will react with triacylglycerol to form the ethyl ester and diacylglycerol [53,49].

It was observed that the opposite also happened; an excessive increase of catalyst also caused a decrease in conversion. This behavior has also been observed in other studies [20,54,55]. According to Tan et al. (2019)[58], this is because an excessive catalyst increase causes exponential glycerol formation and this may have caused a catalyst particle saturation, reducing the contact area between methanol and active sites, causing, thus, a decrease in the biodiesel yield. For Xie and Wang (2019)[57], too much catalyst can increase the viscosity of the reaction mixture, increasing the effective mass transfer resistance of the catalyst and the reagents, resulting, consequently, in a reduction in conversion to biodiesel.

Evaluating the effect of temperature on the reaction, it can be observed, through Fig. 7A and 7B that at low temperatures there were lower conversions to biodiesel, probably because at low temperatures there is less fluidity of the reaction mixture caused by a higher viscosity of palm olein and also the mutual solubility of palm oil and ethanol is reduced. Approaching level +1 of the experimental design, the conversion to biodiesel increases, probably caused by the decrease in the viscosities of the reagents and the increase of oil miscibility in ethanol [57]. After this, following towards the higher temperature level (60 °C) a slight decrease in conversion occurs, perhaps caused by a slight reversible reaction caused by the glycerol present in the mixture [26], since, higher temperatures may accelerate the transesterification rate due to changes in reaction equilibrium [57].

Observing the effect of molar ratio on the transesterification reaction through Fig. 7B e 7C, it was initially noted a positive linear effect of this variable until 1:16. From then, a negative effect was observed probably caused by a decrease in the driving forces between ethoxide and triacylglycerol, caused by excess of ethanol present in the liquid phase where triacylglycerol molecules are dispersed. As explained above, the ethoxide formed after adsorbing onto the catalyst surface returns to the liquid phase where it will react with the triacylglycerol molecule and form an ethyl ester molecule and a diacylglycerol molecule. However, as triacylglycerol molecules are farther apart from each other caused by the presence ethanol in excess, ethoxide will have to travel a longer distance to reach hydrophobic molecules, increasing the time to react and, as a consequence, the conversion to FAEE decreases. The same behavior was observed in other studies found in the literature [21,55,59,60].

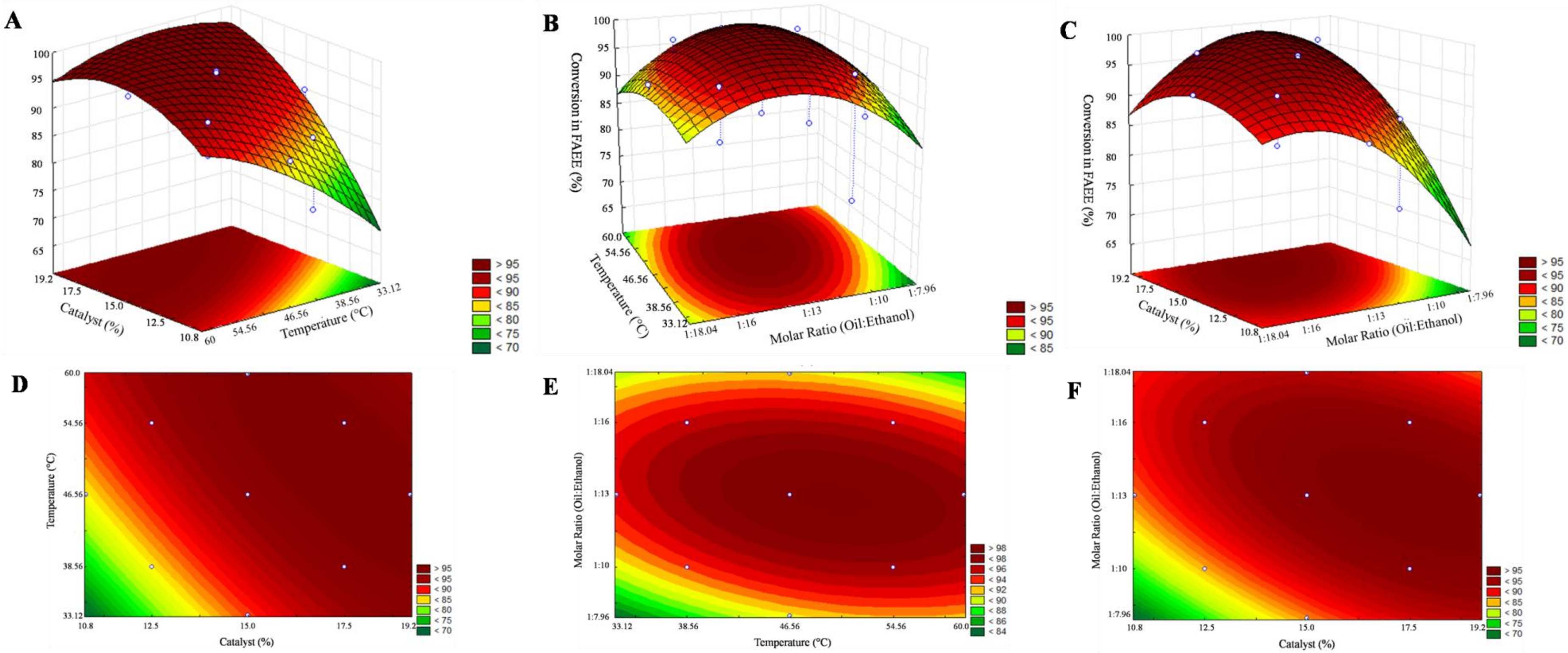

Fig. 7. Response Surfaces: catalyst (%) x Molar Ratio (oil:ethanol) (A); Catalyst (%) x Temperature (°C) (B); Temperature (°C) x Molar Ratio (oil:ethanol) (C) and contour curves: catalyst (%) x Molar Ratio (oil:ethanol) (D); Catalyst (%) x Temperature (°C) (E); Temperature (°C) x Molar Ratio (oil:ethanol) (F). Fig. 6A and 6D were generated by setting the coded variable oil:ethanol molar ratio at level 0 (1:13); Fig. 6B and 6E were generated by setting the coded variable catalyst (%) at level +1 (17.5 %); and the Fig. 6C e 6F were generated by setting the coded variable temperature at level 0.44 (50.1 °C).

4. Conclusions

The present study showed that the use of response surface methodology was very useful to optimize the variables for high conversion FAEE production. Through the optimized variables, it was possible to obtain a conversion of approximately 98 % to ethyl esters using 17.5 % catalyst, 50.1 °C, oil:ethanol molar ratio of 1:13 and 400 rpm stirring during 10 hours of reaction. In addition, no effect of agitation on resin particle morphology was observed. In conclusion, under the studied conditions, despite the long reaction time, Purolite A503S anion exchange resin presents itself as a potential heterogeneous catalyst for use in transesterification reactions and combined with the use of ethanol as a solvent, can produce biodiesel less harmful to the environment when compared to methanol, which is toxic and non-renewable.

Acknowledgement

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CAPÍTULO 5

-DISCUSSÃO GERAL-

1 DISCUSSÃO GERAL

No artigo de revisão intitulado “Heterogeneous catalysts for biodiesel production: a review” (Capítulo 3) foi observado que as condições ótimas para temperatura, razão molar álcool:óleo, concentração de catalisador, velocidade de agitação e tempo de reação mudam para cada tipo de catalisador heterogêneo usado no processo de produção de biodiesel.

Para as resinas de troca iônica, foi observado que parâmetros intrínsecos como densidade de *crosslinking*, porosidade e grau de *swelling* também possuem influência na atividade catalítica. Na avaliação dos resultados, foi observado que as resinas de troca aniônica são mais eficientes usando baixas temperaturas, isso porque elas possuem baixa estabilidade térmica (aproximadamente 60 °C). E isso, em termos de processo, torna-se importante na redução de custos de energia, podendo, talvez, viabilizar a produção de biodiesel utilizando esses catalisadores. A temperatura mais alta utilizada para esse tipo de catalisador foi de 65 °C para a resina Amberlyst A26 OH. Geralmente, tempos longos, maiores que 6 horas, são necessários para se obter altas conversões. Para maiores informações, uma discussão geral mais detalhada encontra-se no próprio trabalho.

Nos experimentos contidos no artigo intitulado “Optimization of the production of biodiesel from palm olein using strongly basic anionic resin as heterogeneous catalyst” (Capítulo 4), observou-se uma redução na a velocidade de reação para a produção de biodiesel utilizando a resina Purolite A503S reduziu bastante a partir de 10 horas de reação. Avaliando o efeito da agitação, não foi observado efeito na morfologia das partículas da resina. Observado o efeito da agitação na conversão em ésteres etílicos, a rotação de 250 rpm foi suficiente para eliminar o efeito da resistência externa à transferência de massa, no entanto, a agitação de 400 rpm foi a escolhida para a realização deste trabalho devido a uma melhor distribuição das partículas no reator e, assim, garantir o melhor contato entre os reagentes e o catalisador.

A partir da análise dos resultados do planejamento experimental, foi observado que o modelo obtido foi significativo e preditivo para descrever os dados experimentais. As variáveis com efeitos significativos para o planejamento realizado foram as variáveis lineares para concentração de catalisador e temperatura e os termos quadrático e linear para razão molar óleína de palma:etanol. Os demais termos, não foram considerados estatisticamente significativos a 5 % de significância, no entanto, optou-se por deixá-los no modelo e não fazer a reparametrização, pois o delineamento experimental teve como principal objetivo encontrar a melhor condição para a reação de transesterificação.

As variáveis foram otimizadas pela máxima conversão em ésteres etílicos e o mesmo ponto foi usado para validação experimental do modelo. Foi observada uma conversão de 98 % em biodiesel utilizando 17,5 % de catalisador, temperatura de 50, 1°C , razão molar oleina de palma:etanol de 1:13, durante 10 horas de reação e agitação de 400 rpm, este valor foi próximo ao predito pelo modelo (99,15 %), mostrando que a validação experimental do modelo foi satisfatória.

CAPÍTULO 6

-CONCLUSÃO GERAL-

1 CONCLUSÃO GERAL

Este trabalho abordou diferentes condições reacionais para diferentes catalisadores. Destacando as condições ótimas de temperatura, concentração de catalisador, razão molar óleo:álcool, velocidade de agitação e tempo de reação para cada tipo de catalisador heterogêneo. Assim como, os mecanismos de reações encontrados na literatura. Foi observado que as resina de troca aniônica apresentaram melhores desempenhos quando comparado aos outros catalisadores heterogêneos para produção de biodiesel e que, para as reações de transesterificação utilizando esses catalisadores, a primeira etapa se dá com a adsorção do álcool pela resina.

A aplicação da metodologia de superfície de resposta para otimização das variáveis pela máxima conversão em ésteres etílicos se mostrou muito útil e a utilização da resina aniônica fortemente básica Purolite A503S combinada com o uso do etanol como solvente, se mostrou um catalisador heterogêneo em pontencial para produzir um biocombustível mais ambientalmente amigável, quando comparado com o metanol, que é tóxico e produzido principalmente por fonte não renovável.

2 TRABALHOS FUTUROS

- Validar metodologia para quantificação de glicerol utilizando cromatógrafo de íons;

- Modelar a cinética de reação utilizando a condição otimizada encontrada neste trabalho;

- Avaliar a capacidade de regeneração e reutilização da resina Purolite A503S.

CAPÍTULO 7

-REFERÊNCIAS BIBLIOGRÁFICAS-

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APÊNDICE

METODOLOGIA PARA QUANTIFICAÇÃO DE COMPONENTES GRAXOS E ETANOL

Para a quantificação dos componentes graxos (TAG, DAG, MAG e FAEE) e etanol, o método cromatográfico HPSEC foi utilizado de acordo com a metodologia descrita por Kittirattanapiboon e Krisnangkura (2008) e Aryee et al. (2011)(ARYEE *et al.*, 2011;ARYEE *et al.*, 2011), usando um cromatógrafo líquido de alta eficiência (HPLC Shimadzu, modelo LC20AT, Japão), com injetor automático (Shimadzu, 20AT, Japão) equipado com um detector de índice de refração (RID). Uma coluna de exclusão de tamanho 100Å PhenogelTM (Phenomenex, Torrance, CA, EUA)(300 × 7,8 mm de diâmetro interno x 5 mm), acoplada a um forno aquecido a 40 °C, foi utilizada para a separação cromatográfica dos compostos. Inicialmente, foi preparada uma fase móvel com 0,25 % (v/v) de ácido acético em tolueno (pureza HPLC). Após a preparação da fase móvel, a coluna foi equilibrada e eluída usando uma vazão de 1 mL/min, em modo isocrático. Para o equilíbrio, a vazão foi aumentada no intervalo 0,2 mL/min a cada 3 min até atingir uma vazão de 1 mL/min, para evitar um aumento brusco da pressão e possível rompimento da coluna.

Para análise dos produtos da reação de transesterificação, foi coletado aproximadamente 0,1 mL com o auxílio de uma seringa de 1 mL, massa entre 40 a 70 mg, no máximo. A amostra foi diluída em 5 mL de tolueno (pureza HPLC). Para quantificação dos componentes, alíquotas de 20 µL foram injetadas no sistema HPLC. O tempo de execução da análise para cada amostra foi de 17 min.

A identificação de cada componente foi realizada de acordo com o tempo de retenção da classe de compostos como mostra a Figura 1.

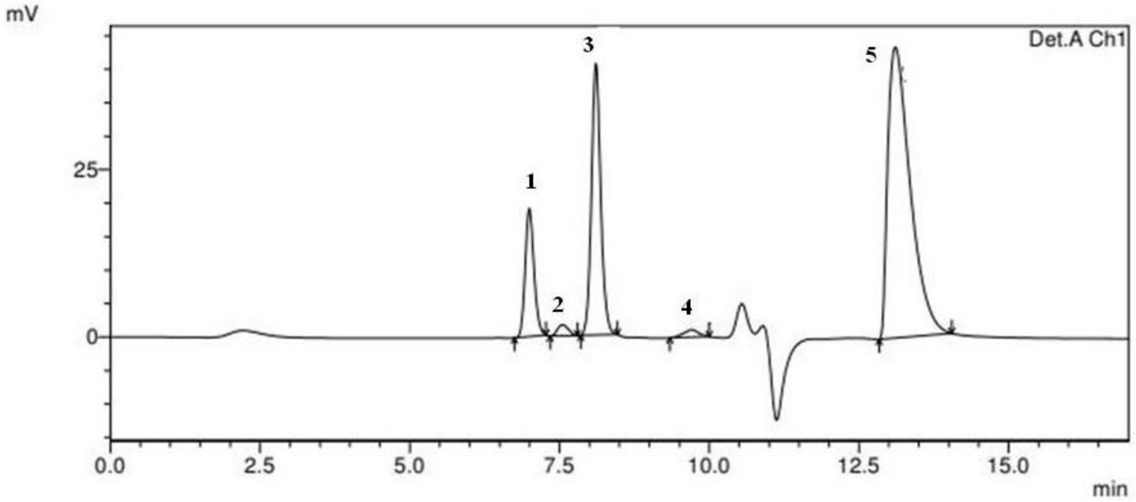

Figura 1. Cromatograma dos componentes da mistura de acilgliceróis, éster etílico e etanol. 1-Triacilglicerol (TAG); 2- Diacilglicerol (DAG); 3-Éster etílico (FAEE); 4-Monoacilglicerol (MAG); 5-Etanol.

A quantificação dos componentes foi realizada a partir de cinco curvas padrão, preparadas com padrões externos de TAG, DAG, MAG, etanol (descritas na Tabela 2, do Capítulo 4) e biodiesel etílico purificado. As concentrações e os valores de área desses cinco componentes foram correlacionados por regressões lineares, utilizadas para quantificações posteriores como mostra a Figura 2. O biodiesel etílico foi obtido de acordo com Silva et al. (2009) (SILVA *et al.*, 2009) a partir de uma reação homogênea utilizando oleína de palma, etóxido de sódio (21%) como catalisador, razão molar óleo:etanol de 1:16, temperatura de 60 ° C, 1% (m/m) de catalisador em relação à massa de óleo, submetido a agitação de 400 rpm por 30 min. Após a reação, o biodiesel foi purificado de acordo com a metodologia descrita por Silva et al. (2009),

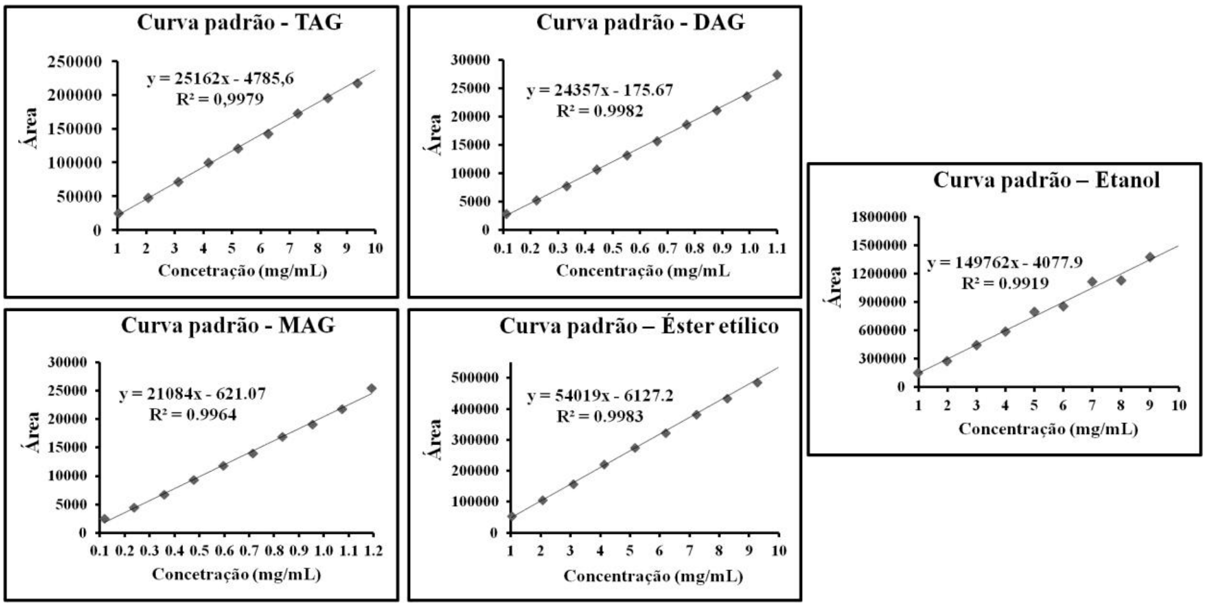

Figura 2. Curvas padrão dos componentes. y = área do cromatograma, x = concentração em mg/mL.

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