STUDY OF THE APPLICATION OF CHOLINE HYDROXIDE AS A CATALYST IN BIODIESEL PRODUCTION

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To my father Ahmed

To my mother Fatma

All my thanks!

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ABSTRACT

Due to the finite stock of fossil fuels and its negative impact on the environment, many countries across the world are now leaning toward renewable energy sources like solar energy, wind energy, biofuel, hydropower, geothermal and ocean energy to ensure energy for the society development security. Biodiesel is one type of biofuel that is renewable, biodegradable and has similar properties of fossil diesel fuels.

Biodiesel is a mixture of fatty acids methyl esters (FAMEs) and can be produced through esterification of fatty acid mixtures or transesterification of vegetable oils and animal fats, using homogeneous and heterogeneous catalysts. Ionic liquid (IL) based catalysts are more and more used since they can be recovered and reused and can have the ability to catalyze both esterification and transesterification reactions. Thus, these types of catalysts, represent clear environmental and safety advantages in relation to classical catalysts.

The present work aims to study the use of choline hydroxide (ChOH) IL as a potentially reusable catalyst for the production of biodiesel. A kinetic study was carried out for the transesterification of a previously characterized vegetable oil sample, with methanol, under the specific conditions: 2 wt.% catalyst dosage, 1:10 oil/methanol molar ratio, for the reaction times of 10, 20, 30, 45, 60 and 120 minutes at 65, 55, 45, and 35 ℃. Transesterification with ChOH provided a 95.7% conversion in FAME content for 30 min of reaction at 65 ℃. The results of the kinetic study demonstrated that the first-order model was generally the best fit for the reaction kinetics considering all the temperatures, with a rate constant (k) estimated as 0.1182 min^{-1} for 65 ℃, and an estimated activation energy of 13.64 kJ/mol.

An activation of LDHs by intercalation was made with 0 (blank test), 1, 2, 4 and 5 wt% of IL (BMIM HSO_4).

The activation of LDH by intercalation with BMIM HSO_4 was not successful, because the conversion values are very low.

Keywords: Biodiesel production; Transesterification; Esterification; Ionic liquid; Choline Hydroxide; LDH; BMIM HSO_4.

RESUMO

Devido à quantidade finita de combustíveis fósseis e do impacto negativo que têm sobre o meio ambiente, muitos países estão a direcionar-se para a utilização de fontes de energia renováveis como energia solar, energia eólica, biocombustível, energia hidroelétrica, energia geotérmica e energia dos oceanos no sentido de garantir energia para o desenvolvimento e segurança da sociedade. O biodiesel é um tipo de biocombustível renovável, biodegradável e com propriedades semelhantes às do diesel.

O biodiesel é uma mistura de ésteres metílicos de ácidos gordos (FAMEs) e pode ser produzido por esterificação de misturas de ácidos gordos ou transesterificação de óleos vegetais e gorduras animais, utilizando catalisadores homogéneos e heterogéneos. Os catalisadores à base de líquidos iónicos (IL) são cada vez mais usados, uma vez que podem ser recuperados e reutilizados, havendo ainda a possibilidade de catalisarem reações de esterificação e transesterificação. Assim, este tipo de catalisadores representa claras vantagens ambientais e de segurança relativamente aos catalisadores clássicos.

O presente trabalho tem como objetivo estudar a utilização do hidróxido de colina (ChOH) como catalisador, potencialmente reutilizável, para a produção de biodiesel. Foi realizado um estudo cinético para a transesterificação de uma amostra de óleo vegetal previamente caracterizada, com metanol, nas condições específicas: 2% (m/m) de catalisador, razão molar óleo / metanol 1:10, para os tempos de reação de 10, 20, 30, 45, 60 e 120 minutos a 65, 55, 45 e 35 °C. A transesterificação com ChOH permitiu obter uma conversão de 95,7%, em termos de conteúdo de FAMEs, ao fim de 30 minutos de reação a 65 °C. O modelo cinético de primeira ordem é o que resulta num melhor ajuste para os resultados experimentais obtidos a todas as temperaturas estudadas. Com este modelo obteve-se uma constante cinética (k) estimada em 0,1182 min^{-1} para 65 °C, e uma energia de ativação estimada de 13,64 kJ/mol.

Uma ativação de LDHs por intercalação foi feita com 0 (teste em branco), 1, 2, 4 e 5% em peso de IL (BMIM HSO_4).

A ativação do LDH por intercalação com BMIM HSO_4 não teve sucesso, pois os valores de conversão são muito baixos.

Palavras-chave: Produção de biodiesel; Transesterificação; Esterificação; Líquido iónico; Hidróxido de colina; LDH; BMIM HSO_4.

نبذة مختصرة

نظرًا للمخزون المحدود من الوقود الأحفوري وتأثيره السلبي على البيئة، تميل العديد من البلدان في جميع أنحاء العالم الآن نحو مصادر الطاقة المتجددة مثل الطاقة الشمسية وطاقة الرياح والوقود الحيوي والطاقة الكهرومائية والطاقة الحرارية الأرضية وطاقة المحيطات لضمان الطاقة لتنمية المجتمع الأمان. وقود الديزل الحيوي هو أحد أنواع الوقود الحيوي المتجدد والقابل للتحلل الحيوي وله خصائص مماثلة لوقود الديزل الأحفوري.

ويمكن إنتاجه من خلال أسترة (FAMEs) وقود الديزل الحيوي هو خليط من الأحماض الدهنية استرات الميثيل مخاليط الأحماض الدهنية أو الأسترة التحويلية للزيوت النباتية والدهون الحيوانية، باستخدام محفزات متجانسة بشكل متزايد حيث يمكن استعادتها وإعادة (IL) وغير متجانسة. يتم استخدام المحفزات القائمة على السائل الأيوني استخدامها ويمكن أن يكون لها القدرة على تحفيز تفاعلات الأسترة والأسترة التبادلية. وبالتالي، فإن هذه الأنواع من المحفزات، تمثل مزايا بيئية ومزايا سلامة واضحة فيما يتعلق بالمحفزات التقليدية.

كمحفز يمكن إعادة استخدامه لإنتاج (ChOH) IL يهدف العمل الحالي إلى دراسة استخدام هيدروكسيد الكولين وقود الديزل الحيوي. تم إجراء دراسة حركية للأسترة التبادلية لعينة زيت نباتي مميزة سابقًا، مع الميثانول، تحت ظروف محددة: 2 وزن٪ جرعة محفز، 1:10 زيت / ميثانول نسبة مولارية ، لأوقات تفاعل 10 ، 20 ، 30 و 45 تحويل 95.7٪ في ChOH مع Transesterification و 60 و 120 دقيقة عند 65 و 55 و 45 و 35. قدمت لمدة 30 دقيقة من التفاعل عند 65. أظهرت نتائج الدراسة الحركية أن نموذج الدرجة الأولى كان FAME محتوى يقدر بـ (k) الأنسب بشكل عام لحركية التفاعل مع الأخذ في الاعتبار جميع درجات الحرارة، مع معدل ثابت 0.1182 دقيقة -1 لـ 65 °C، وطاقة تنشيط مقدرة تبلغ 13.64 كيلوجول / مول.

IL (BMIM عن طريق الإقحام باستخدام 0 (اختبار فارغ) و 1 و 2 و 4 و 5 بالوزن ٪ من LDHs تم تنشيط HSO_4).

ناجحًا ، لأن قيم التحويل منخفضة جدًا BMIM HSO_4 عن طريق الإقحام مع LDH لم يكن تنشيط.

الكلمات الرئيسية: إنتاج وقود الديزل الحيوي؛ الأسترة؛ الأسترة؛ سائل أيوني هيدروكسيد الكولين.

RÉSUMÉ

En raison du stock limité de combustibles fossiles et de son impact négatif sur l'environnement, de nombreux pays à travers le monde se tournent désormais vers les énergies renouvelables comme l'énergie solaire, l'énergie éolienne, les biocarburants, l'hydroélectricité, la géothermie et l'énergie océanique pour assurer l'énergie pour le développement de la société. Sécurité. Le biodiesel est un type de biocarburant renouvelable, biodégradable et qui possède des propriétés similaires à celles des carburants diesel fossiles.

Le biodiesel est un mélange d'esters méthyliques d'acides gras (FAME) et peut être produit par estérification de mélanges d'acides gras ou transestérification d'huiles végétales et de graisses animales, en utilisant des catalyseurs homogènes et hétérogènes. Les catalyseurs à base de liquide ionique (IL) sont de plus en plus utilisés car ils peuvent être récupérés et réutilisés et peuvent avoir la capacité de catalyser à la fois des réactions d'estérification et de transestérification. Ainsi, ces types de catalyseurs, représentent des avantages environnementaux et de sécurité évidente par rapport aux catalyseurs classiques.

Le présent travail vise à étudier l'utilisation de l'hydroxyde de choline IL (ChOH) comme catalyseur potentiellement réutilisable pour la production de biodiesel. Une étude cinétique a été réalisée pour la transestérification d'un échantillon d'huile végétale préalablement caractérisé, avec du méthanol, dans les conditions spécifiques : dosage de catalyseur de 2% en poids, rapport molaire huile / méthanol 1:10, pour les temps de réaction de 10, 20, 30, 45, 60 et 120 minutes à 65, 55, 45 et 35 °C. La transestérification avec ChOH a fourni une conversion de 95,7% de la teneur en FAME pendant 30 min de réaction à 65. Les résultats de l'étude cinétique ont démontré que le modèle de premier ordre était généralement le meilleur ajustement pour la cinétique de réaction compte tenu de toutes les températures, avec une constante de vitesse (k) estimée à 0,1182 min^{-1} pour 65 °C, et une énergie d'activation estimée de 13,64 kJ/mol.

Une activation des LDH par intercalation a été faite avec 0 (test à blanc), 1, 2, 4 et 5 % en poids d'IL (BMIM HSO_4). L'activation de la LDH par intercalation avec BMIM HSO_4 n'a pas réussi, car les valeurs de conversion sont très faibles.

Mots clés: Production de biodiesel; Transestérification; Estérification; Liquide ionique; Hydroxyde de choline; LDH; BMIM HSO_4.

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NOMENCLATURE

Acronyms and symbols

ASTM	American Society for Testing and Materials
DG	Diglyceride
Ea	Activation energy (kJ/mol)
EGR	Exhaust gas recirculation
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GC	Gas chromatography
GC-FID	Gas chromatograph with flame ionization detector
GHG	Greenhouse gas
GL	Glycerol
IL	Ionic liquid
LDH	Layered double hydroxide
MG	Monoglyceride
OA	Oleic Acid
R^2	Coefficient of determination
SFO	Sunflower oil
TGL	Triglycerides
T	Temperature
TAG	Triacylglycerol
WCO	Waste cooking oil
WFO	Waste frying oil
Wt	Weight

Formulas

[BMIM]HSO_4	1-butyl-3-methylimidazolium hydrogen sulfate
[BMIM][$FeCl_4$]	1-butyl – 3-methylimidazolium tetrachloroferrite
[BSMBIM][CF_3SO_3]	3-methyl-1-(4-sulfo-butyl)-benzimidazolium Trifluoromethanesulfonate
ChOH	Choline hydroxide
EtOH	Ethanol
H_2SO_4	Sulfuric acid
KOH	Potassium hydroxide
MeOH	Methanol
NaOH	Sodium hydroxide
NOx	Oxides of nitrogen

1. BACKGROUND AND OBJECTIVES

1.1. BACKGROUND

Need for energy is continuously growing due to fast industrialization and metropolitan growth. The main energy resources are petroleum, coal and natural gas and due to the non-renewable nature, these energy sources are diminishing day by day. Newly, the petroleum prices have been setting record high in the history as a result of heavy dependence on petroleum as a major source of fuel or transportation and electricity generation [1].

The overall battles to support the move from non-renewable fuels to the sustainable and condition amicable biofuels led to numerous investigations to build up an elective property fluid fuel. Due to these research biodiesels have been recognized as a manageable and cleaner elective fuel that will help in diminishing the world's temperature by decrease in the release of the ozone harming substances like CO_2, NOx and SO_2 [2].

Biofuels are very attractive option to overcome the energy crisis since waste feedstock´s are accessible freely or almost freely for the production of biofuels (biodiesel, bioethanol, biogas etc…) by different chemical and biological conversion technologies [3]. The biofuelproduction is increasing globally, which is able develop in coming years due to continuous dwindling of fossil fuel reserve [4]. Among different types of biofuels, biodiesel is getting more attraction due to its properties and chemical nature, which can be used as blend with diesel fuel [5]. To utilize the biodiesel as fuel, no motor modification is required for [6] and in contrast to conventional petroleum diesel, the biodiesel is a clean, secure and non-hazardous due to this biodegradability, renewable and carbon neutral nature [7].

1.2 OBJECTIVES

1.2.1 Main objective

The main objective of this Master thesis is to study the production of biodiesel using ionic liquids as catalyst. Choline hydroxide was used as an alkaline IL and an heterogenous catalyst based on a layered double hydroxide (LDH) was also used.

1.2.2 Specific objectives

- Study of biodiesel production using a vegetable oil and methanol as reactants, evaluating the reaction kinetic parameters (kinetic constant and activation energy) of the esterification reaction catalyzed by ChOH;

- Assess the performance of a layered double hydroxide (LDH) Mg-Al-CO_3 activated by intercalation of 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4, as heterogeneous catalysts for the esterification reaction of oleic acid.

1.3 Document Structure

This master thesis report is organized into four chapters. Chapter 1 presents a brief background and relevance of the work, as well as the description of the objectives supporting the interest and novelty of the studied strategies.

In order to situate the field of biodiesel production nowadays, Chapter 2 presents an presents an overview about biodiesel. In addition, it contains the advantages and disadvantages of using biodiesel, its physicochemical properties, current and advanced production methods of this biofuel.

Also it presents a review of the application of ionic liquids in the production of biodiesel, as well as some published works on recovery of ionic liquids and then, an introduction to the ionic liquids chosen for this work. Besides that, the chapter presents a review of some published work on the kinetic study of transesterification of waste cooking oil, and it brings a brief outline of all the works done so far by the research group with a focus on the production of biodiesel using ionic liquids as catalysts, and presents an overview about heterogeneous catalysts, their types, advantages, and disadvantages.

Concerning the experimental section, Chapter 3 describes the equipment, reagents, and experimental procedures, highlighting the process for the transesterification reaction of the sunflower oil and also the activation of LDHs by intercalation of ionic liquid.

With respect to the experimental results obtained and the appropriate discussion on the kinetic study with ChOH ionic liquid and the use of LDH as a heterogeneous catalyst are presented in Chapter 4.

Finally, Chapter 5 summarizes the main conclusions as well as the suggestions for future research.

2. BIODIESEL

Diesel motors are considered the most efficient as far as interior burning and cost. They likewise transmit generally low degrees of carbon dioxide, however they discharge elevated levels of particulates and oxides of nitrogen (NOx). As an option in contrast to diesel oil, biodiesel has been investigated by several researchers [8].

Biodiesel could be a fluid fuel comprising of mono alkyl esters (methyl or ethyl) of long chain greasy acids determined from vegetable oils or animal fats or micro and macro algal oil. Biodiesel, is additionally, the title given to fuel for diesel motors made by the chemical transformation of animal fats or vegetable oils. It can moreover be characterized as a biofuel comprising of mono-alkyl esters of long chain greasy acids, created from renewable bio-lipids by means of transesterification process [9].

What's more, biodiesel gives better lubricity, which advances the smooth activity of motor parts, lessens motor wear, and drags out motor lifetime. Biodiesel is ecologically well disposed, maintainable, biodegradable, non-combustible, and non-harmful. These properties make biodiesel a standout amongst other elective energizes for making sure about future energy prerequisites [10].

2.1 ADVANTAGES AND DISADVANTAGES OF BIODIESEL

The biodiesel has numerous benefits as well as some shortcoming, which have been listed below. The major benefits of using biodiesel as a fuel is [11]:

- Biodiesel produces less outflows, for example, CO_2, CO, SO_2, particulate matter (PM) and hydrocarbons (HC) contrasted with diesel.
- Delivering biodiesel is simpler than diesel and less time consuming.
- Biodiesel can cause the vehicle to perform better as it has higher cetane number.
- Biodiesel prolongs motor life and diminishes the requirement for upkeep.
- It very well may be utilized without including extra oil, in contrast to diesel motor.
- Biodiesel holds an incredible potential for animating manageable country advancement and an answer for energy security issue.
- Biodiesel should not be penetrated, shipped, or refined like diesel.

- Biodiesel is more cost effective than diesel since it is delivered locally
- Biodiesel should not be penetrated, shipped, or refined like diesel.
- Biodiesel is better than diesel fuel with respect to sulfur content, flash point, aromatic content, and biodegradability.
- It is more secure to deal with, being less harmful, increasingly biodegradable, and having a higher flash point.
- Non-combustible and non-harmful, diminishes tailpipe discharges, noticeable smokeand toxic exhaust and scents.
- No necessary motor adjustment up to B20 (a mixture composed of 20% of biodieselwith 80% of diesel).
- Higher ignition effectiveness, portability, availability, and inexhaustibility of biodiesel.

There are also some disadvantages of using biodiesel that must be taken intoconsideration:

- It transmits higher NOx emanation than diesel.
- Higher pour and cloud point fuel freezing in chilly climate causing a chilly climate beginning.
- Biodiesel has a corrosive nature against copper and brass.
- Biodiesel lower motor speed and force. The biodiesels on the normal abatement powerby 5% contrasted with that of diesel at evaluated load.
- Coking of injectors on the piston and top of the motor.
- Biodiesel debasement under storage for delayed periods.
- The high viscosity, in long haul activity, introduces the formation of injector deposits, plugging of filters, lines and injectors, ring sticking and contradiction with conventional.
- Greasing up oils. Carbon stores on piston and top of the motor.
- Biodiesel causes exorbitant motor wear.

2.2 RAW MATERIALS FOR BIODIESEL PRODUCTION

In available literature there are various feedstocks reported which can be utilized to produce biodiesel. Among them, soybean, palm, sunflower, rapeseed and peanut oils have been considered in earlier times but their negative affect on food crops have hindered their usage. The choice of raw material mainly depends upon the availability and cost. European communities for example are self-dependent in production of edible oil with surplus to export. As a result, edible oils such as rapeseed is commonly used in European Nations' biodiesel. In America, soybeans are commonly used. Additionally, countries with coastal areas such as Malaysia, Indonesia and Thailand have surplus palm, coconut oils which are used for biodiesel. In Brazil, the mostly used oils are soybean, castor and palm kernel. In India, Jatropha and Karanja have been reported to be as prominent sources for biodiesel production [12].

2.2.1 Edible oils (1st generation)

Within the appearance of biodiesel time, broad utilization of edible oils is profoundly recognizable crude materials for biodiesel production. Subsequently the edible oils derived from feedstocks like soybean, mustard, rice, wheat, coconut, rapeseed, olive, palm, corn etc are categorized as first-generation feedstocks of biodiesel synthesis. Although the first-generation feedstocks possess advantages like accessibility of crops and relatively simple conversion process, the major drawback of this feedstock is the threat of limitation in food supply which may lead to extend in food costs as the fuel is derived from food sources. On the whole, the controversial issue arises that is necessary to prefer one, or the other of ‘food vs fuel’ alternatives. On the other hand, high cost, a restricted region of cultivation and adaptability to climatic conditions also obstruct the utilization of first-generation feedstocks. These difficulties confined the clients to move on to other assets for biodiesel production [13].

2.2.2 Non-edible oils (2nd generation)

Second generation oils are basically non-edible oils inferred from assortment of feedstocks counting lignocellulosic feedstocks and non-food crops. These oils basically incorporate Karanja, *Jatropha curcas*, Polanga, Linseed, *Moringa oleifera*, *Croton megalocarpus*, Jojoba, Chinese fat etc. The advantage of utilizing non-edible oils is that these do not have superfluous burden on food crops in comparison of first-generation oils [14].

2.2.3 Other sources (3rd generation)

In any case of vegetable oils, some other sources like micro algae, waste frying oil, animal fat, fish oil, pyrolysis oil etc constitute third generation source of biofuel. These viable sources of biofuel overcome the challenges confronted by previous generation feedstocks such as accessibility, financial possibility, affecting food chain and adaptability toclimatic conditions. Microalgae can be a potential feedstock for biodiesel production. Since several algal species have the capacity to live in unforgiving conditions, it is best suited to local environments with low culturing cost. Another major advantage of micro algae is the lipid content [13].

Feedstocks for biodiesel production delineates the oil sources suitable for biodiesel production. The non-edible oils feedstocks can be seen as the future sources of biodiesel production compared to edible oils as the latter are competitive to food requirements of people. The former can be obtained from crops cultivated on waste lands in remote areas and demeaned forests. In addition to it, these can be grown on boundaries of agricultural fields, water system canals and roadsides [15]. Some examples of feedstocks for biodiesel production are presented at Table 1.

According to Table 1 we can see that the raw materials used for producing biodiesel present on a large scale like edible oils that presents the big value compared to non-edible oils and other sources.

Table 1. Feedstocks for biodiesel production [15].

Edible oil (1st generation)	**Non-edible oil (2nd generation)**	**Other sources (3rd generation)**
Cottonseed oil	Jatropha oil	Microalgae
Coconut oil	Karanja (Pongamia oil)	Spirulina platensis algae
Sunflower oil	Mahua oil	Waste cooking oil
Canola oil	Neem	Animal fats
Soybean oil	Eucalyptus oil	Beef tallow
Castor oil	Linseed	Poultry fat
Mustard oil	Rubber seed	Fish oil
Peanut oil	Polanga	Chicken fat
	Yellow oleander	*Chlorella protothecoides*

2.3 BIODIESEL PROPERTIES

In recent years, the research, development, and commercialization of biodiesel have been boosted due to the urgency of finding the best solution to the world energy crisis. We cannot proceed to depend heavily on crude petroleum as the essential source of transportation fuels and electricity. In spite of the fact many alternative energies such as solar, wind, biomass, and geothermal, only biofuel or biodiesel can be used on a large scale, especially for transportation, due to its reliability and economic feasibility [16].

There are characteristics of the fuel that are straightly linked to the FAME composition profile, e.g., kinematic viscosity, density, cetane number, calorific value, flash point, cloud point, and pour point.

Both density and viscosity are essential properties for any liquid fuel since they influence the injection system performance. In general, high kinematic viscosity is undesirable because it decreases the injection velocity of biodiesel-blended fuels, and the fuel density determines the precise volume of fuel that needs to be injected into the system. Other important properties are the cetane number which is related to the time delay between the injection and auto-ignition of the fuel, and the acid number which defines the amount of free fatty acids present in the fuel.

The flash point is the temperature at which the fuel will ignite when it is exposed to either spark or flame. Even though the flash point does not have a direct impact on the combustion characteristics, increasing it ensures safe storage and transportation of the fuel. Besides, the cloud point is the temperature at which wax crystals first become visible when the fuel is cooled. The presence of solidified wax thickens the oil, which clogs the fuel filters and injectors in internal combustion engines. In contrast, the pour point is the lowest temperature at which the fuel is still able to flow.

Moreover, the heating value of the fuel indicates the quantity of energy that is released when the unit amount of fuel burns. For an internal combustion engine, fuels with a higher value are advantageous, but biodiesel fuel has a lower heating value when compared to diesel due to its high oxygen content [17].

Table 2 sums up the significant properties of biodiesel dependent on the two standards ASTM D6751 and EN 14214. The utilization of biodiesel altogether lessens the emanations of hurtful greenhouse gas (GHG), particulate issue, and hydrocarbons yet marginally rises fuel utilization and diminishes the motor force. In spite of the fact that NOx outflows are expanded now and again, this can be limited utilizing exhaust gas recirculation (EGR) or different added substances.

Table 2. Properties of biodiesel [16].

Properties	**ASTM D6751**	**EN 14214**
Flash point, min (°C)	100–170	≥120
Cloud point (°C)	−3--12	- *
Pour point (°C)	−15--16	- *
Kinematic viscosity at 40 °C (mm^2/s)	1.9–6.0	3.5–5.0
Specific gravity at 15 ◦C (kg/L)	0.88	0.86–0.90
Density at 15 °C (kg/m^3)	820–900	860–900
Cetane number, min	47	51
Iodine number, max	- *	120
Acid number, max (mg KOH/g)	0.50	0.50
Ash (wt %)	0.02	- *
Sulphated ash, max % (m/m)	0.02	0.02
Oxidation stability, min (h, 110 °C)	3	6
Water and sediment, max (v/v %)	0.05	0.03
Water content, max	0.03 (v/v)	500 (mg/kg)
Free glycerol, max (wt %)	0.02	0.02
Total glycerol, max (%)	0.24	0.25
Sulphur content, max	0.05 wt%	10 mg/kg
Phosphorus content, max	0.001 wt%	10 mg/kg

Each of these properties presented in Table 2 represents a parameter of fundamental importance in determining biodiesel quality. The kinematic viscosity is the representation of flow resistance under gravity, indicating the completion stage of the biodiesel synthesis reaction. The cetane number of a diesel fuel molecule is strictly related to the combustion rate and the level of compression required for the ignition. The lower heating value indicates the amount of heat released by the combustion reaction of a sample of the fuel, and the flash point is the ignition temperature of the fuel [18].

A correlation of biodiesel properties is classified in Table 3. In this table a comparison between biodiesel and petro-diesel is presented. It was affirmed that biodiesel delivered from characteristic and sustainable assets is a magnificent option for existing petro-diesel, particularly for transportation. As appeared in Table 3, biodiesel has better properties than petro-diesel in numerous zones: for instance, higher cetane number (a critical bit of leeway with respect to motor execution and discharges), low debris substance, and low carbon buildup, though different properties can be improved by utilizing blending processes.

Table 3. Comparison between biodiesel and petro-diesel [16].

Properties	**Petro-Diesel**	**Biodiesel from Waste Cooking Oil**
Flash point, min (°C)	67–85	196
Pour point (°C)	-19--13	-11
Kinematic viscosity at 40°C (mm^2/s)	1.9 – 4.1	5.3
Density at 15 °C (kg/m^3)	75–840	897
Cetane number, min	40–46	54
Ash (wt %)	0.008 – 0.010	0.004
Carbon residue (%)	0.35 – 0.40	0.33
Sulphur content (%)	0.35 – 0.55	0.06
Water content (%)	0.02 – 0.05	0.04
Higher heating value (MJ/kg)	45.62 – 46.48	42.65

2.4 METHODS FOR BIODIESEL PRODUCTION

2.4.1 Esterification

Esterification is a process to produce biodiesel. The reaction takes place between a fatty acid, present in plant oil or even pure, and an alcohol to afford an alkyl ester (biodiesel) and water (Figure 1). Esterification normally occurs via acid catalysis. This process is indicated for plant oils with high levels of free fatty acids, where base catalysis is virtually impossible. The reaction is reversible, but slower compared with base catalysis, requiring higher temperatures and longer reaction times to achieve great yields. Esterification can be catalyzed by inorganic acids, like sulfuric acid(H_2SO_4). It is a reversible reaction and an excess of one of the reactants usually the alcohol, or the removal of water is normally undertaken to shift reaction equilibrium toward biodiesel accumulation [19].

The esterification procedure is commonly completed utilizing sulfuric acid on oils having free fatty acid (FFA) content more noteworthy than 2%. During the esterification response, FFA present in oil gets changed over to methyl ester if using methanol and water is delivered as a result [20].

Esterification is an alternative route when the free fatty acid content within the feedstock is high as in the case of *Jatropha curcas* oil, residues of animal fat, and other low-quality crude materials. These sources have lower cost and reasonable availability. In this way, destination to biodiesel production is more convenient than recycling, because such materials are often disposed in inappropriate places [19].

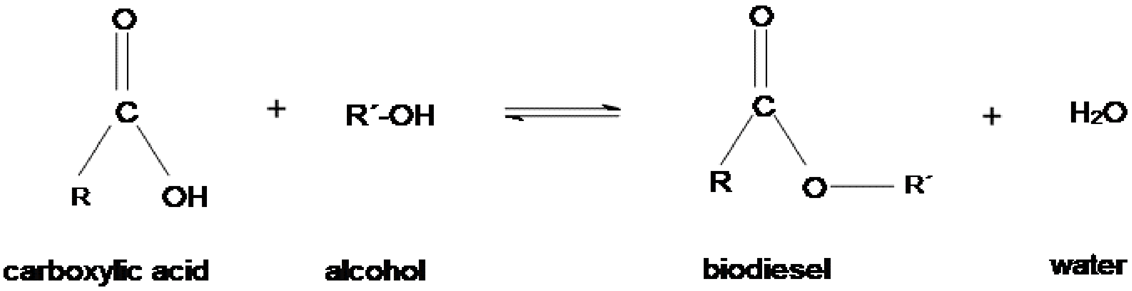


Figure 1. Esterification of carboxylic acid [19].

2.4.2 Transesterification

The transesterification is the most convenient process due to its low cost and simplicity while the selection of feedstock is critical as it accounts about 70% of the total production cost from edible and non-edible sources [21].

Biodiesel is produced by transesterification of triglycerides with short-chain alcohols in the presence of a catalyst. Because of the reversibility of the reaction, it is important to utilize an excess of alcohol to drive the reaction balance. In any case, the transesterification reaction can be done without a catalyst through supercritical process reactions. This process consists of three consecutive reversible reactions where triglycerides are converted into diglycerides, diglycerides are converted into monoglycerides and finally, monoglycerides are converted into glycerol. What's more, for each glyceride that reacts the formation of an ester (biodiesel) molecule occurs [22].

Figure 2 shows the transesterification of a triglyceride with methanol. The reaction preferably takes place with low molecular weight alcohols such as methanol, ethanol, propanol, or butanol. However, methanol is highly used because of its low cost, higher polarity, and easy separation from glycerol. The catalysts employed may be of acidic, basic, or enzymatic nature and can be homogeneous or heterogeneous. Some undesirable reactions may occur during the production of biodiesel.

The presence of water in the reaction medium can lead to hydrolysis of the esters forming free fatty acids and, consequently, soap, which causes problems in the purification of biodiesel (Figure 3). Triglycerides with high concentration of free fatty acids neutralize the basic catalyst and form soap, reducing the yield of biodiesel (Figure 4).

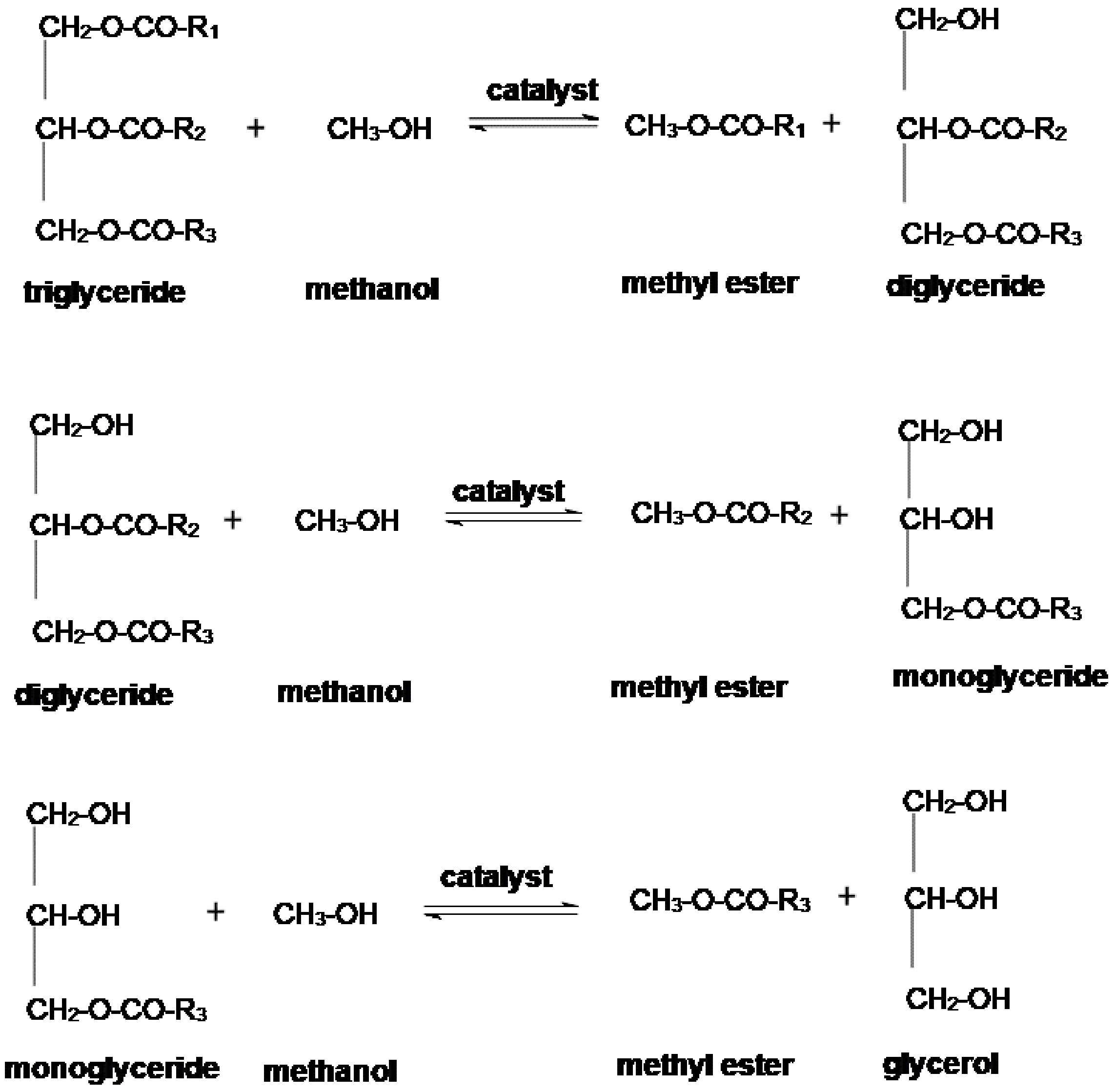


Figure 2. Transesterification of triglycerides with methanol [19].

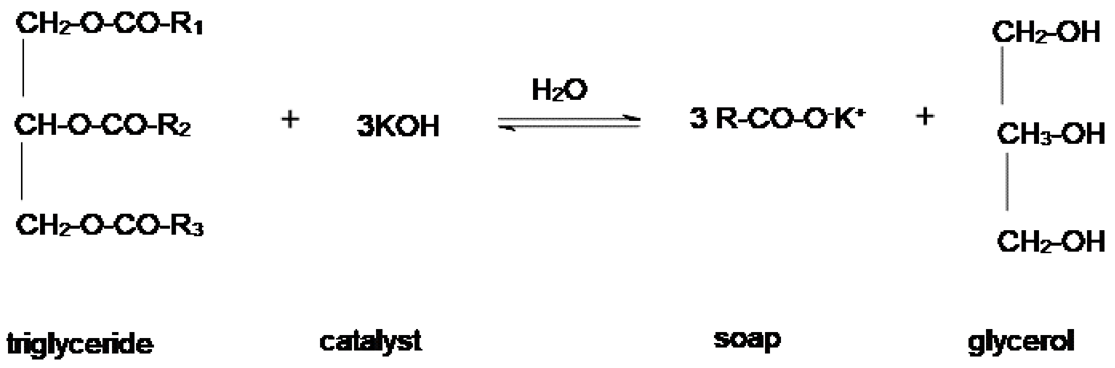
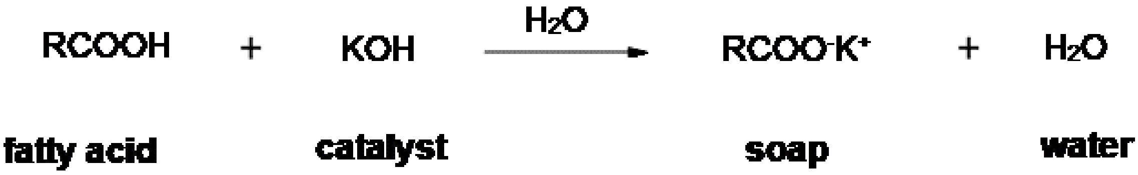


Figure 3. Saponification of triglycerides [19].



$$RCOOH + KOH \xrightarrow{H_2O} RCOO^-K^+ + H_2O$$

Figure 4. Soap formation as a result of free fatty acid neutralization [19].

2.5 CATALYSTS

Catalysts play an important role speeding up biodiesel production processes. Catalysts are utilized in esterification and transesterification processes to facilitate the transformation of the crude material into useful biodiesel. In the absence of catalysts, the esterification and transesterification processes may require longer times, which will expand the general expense of biodiesel production. Catalysts enhance the solubility of alcohol which, in turn, increases the reaction rate [23].

The main catalysts utilized can be classified, as per their chemical presence in the transesterification reaction, as homogeneous or heterogeneous catalysts. Homogeneous catalysts act in the same liquid phase as the reaction blend, while heterogeneous catalysts act in a different phase from the reaction mixture, for the most part as a solid. Heterogeneous catalysts are noncorrosive, a green process and environmentally friendly. They can be recycled and used several times, thus offering a more economic pathway for biodiesel production the preferred alcohol for the production of biodiesel due to its low cost and industrial availability [24]. Figure 5 shows the different types of catalysts that can be used in the transesterification process.

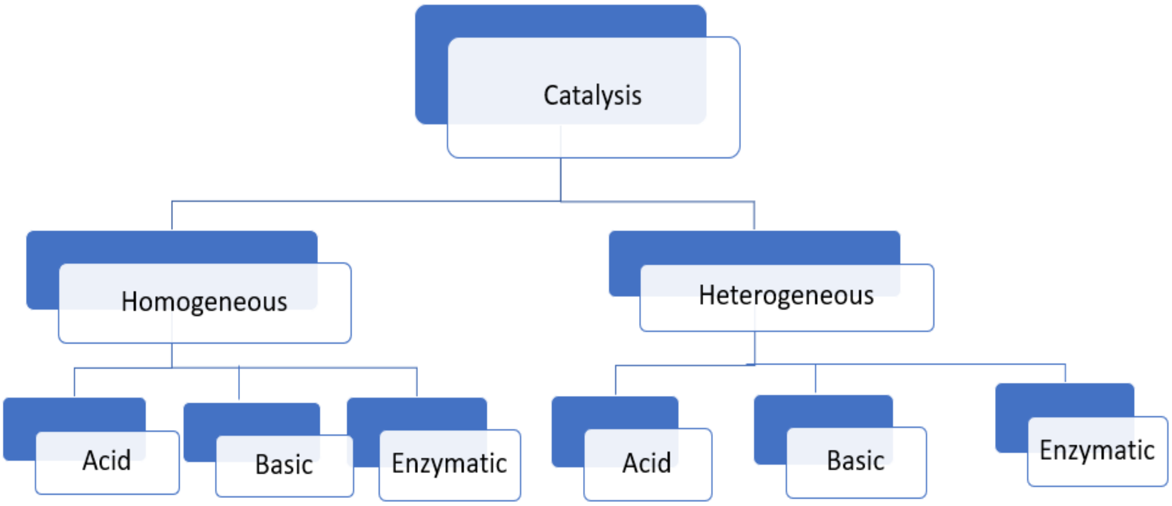


Figure 5. Different types of catalysis employed in the transesterification [22].

In the last decades, there has been a growing interest in the development and employment of new heterogeneous catalysts for biodiesel production. Heterogeneous or solid catalysts can be easily recovered, regenerated and reused. Depending on or their nature they can be basic like alkaline earth metal oxides (CaO, MgO), hydrotalcite, acids like zirconia and alumina-based catalysts or enzymatic, like immobilized lipase [25-26]. Heterogeneous catalysts facilitate continuous reactor operation as they are easily separated from the reaction medium. They also minimize biodiesel and glycerin purification steps [22].

2.5.1 IONIC LIQUIDS

Ionic liquids (ILs) are salts that are in the liquid phase at temperatures underneath 100°C, have low volatility, great chemical and thermal stability and high catalytic activity. They have the advantages of being reused and easily separated from the reaction medium. Ionic liquids are too able of at the same time promoting FFA esterification and transesterification of triacylglycerols [27, 28]. Their main disadvantages are related to the high temperatures utilized with some ionic liquids and the possibility of deactivation due to the glycerol formed [29].

The most interesting characteristic of ionic liquids is the possibility of designing a molecule aiming at a particular application or in order to get a certain set of properties such as melting point, viscosity, density, water solubility and selectivity [30].

The synthesis of ionic liquids is quite simple and, by controlling the synthesis, it is additionally possible to control the purity of the materials formed [31].

Ionic liquids were initially introduced as an alternative green reaction media because of their unique physical and chemical properties. Today they have marched far beyond this border, showing their significant role in controlling the reaction as catalysts. Depending upon the functional group attached to the cation and/or anion, the ionic liquid may behave as an acidic, basic, or organocatalyst.

As acid catalysts the application of acidic (Bronsted as well as Lewis) task specific ionic liquids (TSILs) as a catalytic material is growing rapidly in the field of catalysis. Combining the useful characteristics of solid acids and mineral acids, TSILs have been synthesized to replace the traditional mineral liquid acids, such as hydrochloric acid and sulphuric acid, in the chemical reactions. In view of green chemistry, the substitution of harmful liquid acids by reusable TSILs is one of the most promising catalytic systems in chemistry [31].

As base catalysts basic functionalized ionic liquids have aroused unprecedented interest because they showed more advantages, such as convenient recycling and higher catalytic efficiency than the mixture of inorganic base and ionic liquid for some base-catalyzed processes. Basic ionic liquids have been used to catalyze a number of reactions like aza-Michael addition reaction, Michael addition of active methylene compounds, condensation reaction of aldehydes and ketones with hydroxylamine, synthesis of quinolines, pyrroles.

In the last few years, a renewed interest in the use of organic compounds as catalysts has begun to emerge. Ionic liquids have the potential to have a huge impact in this area. One of the promising approaches to organocatalysis is through hydrogen bonding interactions, and the reactions to which this has been most often applied are Diels-Alder cycloadditions and their derivatives [32].

2.5.2 KINETIC STUDIES OF ESTERIFICATION REACTION

The determination of the kinetic parameters of the esterification reaction of FFAs is additionally interesting, because it permits a better understanding of the suitability of a particular catalyst for biodiesel production. Normally, the main studied kinetic parameter is the activation energy (Ea), defined as the minimum energy required for the reaction to take place. Only when the reactants collide with this minimum energy is that the products are formed. Too, the activation energy is a measure of how the reaction rates are impacted by the temperature. Reactions that have a small activation energy (below 10 kJ/mol) have a little dependency on temperature, whereas reactions with high activation energy (above 60 kJ/mol) have a strong reliance on temperature. Therefore, the lower the activation energy, the easier it is to turn reactants into products. Employing a catalyst is a practical way to diminish the activation energy, as catalysts work by providing a different pathway for the reaction to occur with lower activation energy. The catalyst has no impact on the reaction equilibrium, and therefore the equilibrium is not changed. Too,the catalyst is always regenerated at the end of the process. There are several studies on the literature that focuses on the estimation of the activation energy of both the esterification and the transesterification reactions for biodiesel production [33]. The main studies are summarized on Table 4.

Table 4. Review of kinetic studies regarding biodiesel production [40].

Feedstock	**Alcohol**	**Order**	**Reaction type**	**Catalyst**	**Temperature range (°C)**	**Activation Energy (kJ/mol)**	**Ref.**
Oleic acid	MeOH	1st	Esterification	$[BMIM][FeCl_4]$	40 – 70	17.97	[34]
Waste plum Stone	MeOH	1st	Esterification	H_2SO_4	40 – 60	13.20 – 11.55[a]	[35]
Oleic acid	EtOH	2nd	Esterification	H_2SO_4	75 – 120	36.62	[36]
Palm fatty Acids	MeOH	1st	Esterification	H_2SO_4	130 – 160	6.53 –15.05[a]	[37]
		2nd		CH_3SO_2OH		3.78 –10.12[a]	
Palm oil	MeOH	1st	Esterification	H_2SO_4	55 – 65	75.3	[38]
			Transesterif	KOH		1.45[b] 328[c] 89.3[d]	
Waste cooking oil	MeOH	1st	Transesterif	$[BSMBIM]$ $[CF_3SO_3]$	80 – 140	19.24	[39]

[a] Variation in the catalyst dosage; [b] TGL - DG; [c] DG - MG; [d] MG – GL respectively.

Fauzi and co-workers (2014) investigated the esterification of oleic acid with methanol using the ionic liquid 1-butyl-3-methylimidazolium tetrachloroferrite [BMIM][$FeCl_4$] as a catalyst. The conditions applied were a molar ratio methanol/oleic acid of 22:1; 3 mmol of catalyst loading and a total reaction time of 3.6 h, with sampling every 36 min. The temperature was varied from 40 to 70°C. The change in oleic acid concentration was assessed by titration with a KOH solution. They arrived at the conclusion that the reaction follows pseudo-first order kinetics and estimated the activation energy as 17.97 kJ/mol and a pre-exponential factor as 181.62 min^{-1} [34].

Kostić *et al.* (2016) studied the esterification reaction of waste plum stone with methanol applying sulfuric acid as catalyst. The study was carried out under variation of catalyst loading, methanol/oil ratio, and temperature, modeling the reaction as a pseudo-first order. They concluded that the activation energy suffers a slight diminish when the catalyst dosage increments. The catalyst loading of 0.049 mol/dm^3 leads to an activation energy of 13.20 kJ/mol, while increasing the catalyst loading to 0.172 mol/dm^3 leads to an activation energy of 11.55 kJ/mol, that represents a very small diminish [35].

Neumann *et al.* (2016) examined the esterification reaction of oleic acid with ethanol utilizing sulfuric acid as catalyst. They approached the variation of the concentration of oil by a second order reaction, arriving at an activation energy of 36.62 kJ/mol and a pre-exponential factor of 4.72×10^2 $m^3mol^{-1}s^{-1}$[36].

Aranda *et al.* (2008) studied the esterification reaction of palm fatty acids with methanol applying several acidic catalysts. The two catalysts that displayed the finest comes were sulfuric acid and methane sulfonic acid. The reaction promoted by both catalysts was modeled as a first order reaction related to the oil. They varied the concentration of the catalysts and the temperature, and they found out that the activation energy diminishes as the catalyst stacking increments. For a 0.01wt% catalyst loading, the activation energy was found as 15.05 kJ/mol for the reaction catalyzed by sulfuric acid and 10.12 kJ/mol for the reaction catalyzed by methane sulfonic acid. Increasing the catalyst loading to 0.05 wt% driven to activation energies of 6.53 kJ/mol (sulfuric acid) and 3.785 kJ/mol (methane sulfonic acid) [37].

Jansri *et al.* (2011) investigated the reaction of palm oil with methanol in a two-stage process: esterification reaction of the FFAs with sulfuric acid as catalyst followed by a transesterification reaction of the triglycerides with sodium hydroxide. The overall order of the esterification was assumed as being first order, whereas for the transesterification a second order reaction. The temperature was varied from 55 to 65°C. They found an activation energy of 75.3 kJ/mol for the esterification reaction. For the transesterification reaction, they estimated the activation energies for each step of the reaction: conversion of triglycerides (TGL) into diglyceride (DG) (1.45 kJ/mol), diglyceride into monoglyceride (MG) (328 kJ/mol) and monoglyceride into glycerol (GL) (89.35 kJ/mol) [38].

Ullah *et al*. (2017) studied the transesterification reaction between waste cooking oil and methanol with ionic liquid 3-methyl-1-(4-sulfo-butyl)-benzimidazolium trifluoromethanesulfonate [BSMBIM][CF_3SO_3]. They simplified the reaction by ignoring the intermediates of the transesterification reaction, modeling the reaction as a first order. The temperature range studied was from 80 to 140°C and they estimated an activation energy of 19.24 kJ/mol [39].

2.5.3 HETEROGENEOUS CATALYSTS

Homogeneous catalysts have the main advantage of acting in the same phase of the reaction mixture, so the mass transfer resistance is minimized. Depending or their nature they can be basic, acid or enzymatic. Currently, the most common catalysts employed in the biodiesel industry are the homogeneous basic ones, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) that are easily soluble in methanol [23]. Homogeneous basic catalysts, having a higher reaction rate than homogenous acid ones, have the advantage of high biodiesel yield achieved in short reaction time under mild operating conditions [22].

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 utilization of acidic and alkaline homogeneous catalysts. The fundamental reasons by which heterogeneous catalysts have received extraordinary consideration is the way that they are non-corrosive, can be recovered, reused, applied in continuous processes, and have easy separation of the obtained product [41]. Heterogeneous catalysis is a choice to produce biodiesel without creating watery wastes. It can be performed in batch or continuous processes without requiring additional purification steps, and high yields of high-quality biodiesel can be obtained. A key favorable position of this catalysis is that it permits playing out the esterification of free fatty acids and triglyceride transesterification at the same time, and along these lines diminishes time and energy utilization [42]. A literature survey on advantages and disadvantages of heterogeneous catalysis is presented in Table 5.

Table 5. Advantages and disadvantages of heterogeneous catalysts used for transesterification reaction [22].

Advantages	Disadvantages
Easily recovered, regenerated and reused Available to batch or continuous fixed bed reactors	Lower conversions requiring more severe reaction conditions to achievethe same conversions of homogeneous ones
Requires fewer process units with asimpler separation and purification processes The amount of water is reduced Base catalysts are more active than acidAcid catalysts are not affected by the FFA or water amount,	Mass transfer resistance due to the presence of three phases (oil/alcohol/catalyst) in the reaction mixture
Capacity to catalyzed both transesterification and esterification reaction	Base catalysts are affected by high FFA and water content

Heterogeneous catalysts have many physical and chemical properties which directly affect the biodiesel yield and quality as shown in Figure 6. These properties are mainly responsible for the performance of transesterification reaction in biodiesel production and investigated by different techniques such as XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy) SEM (scanning electron microscopy), BET (Brunauer–Emmett–Teller), TGA (thermogravimetric analysis) and Hammett basicity method, etc… [43].

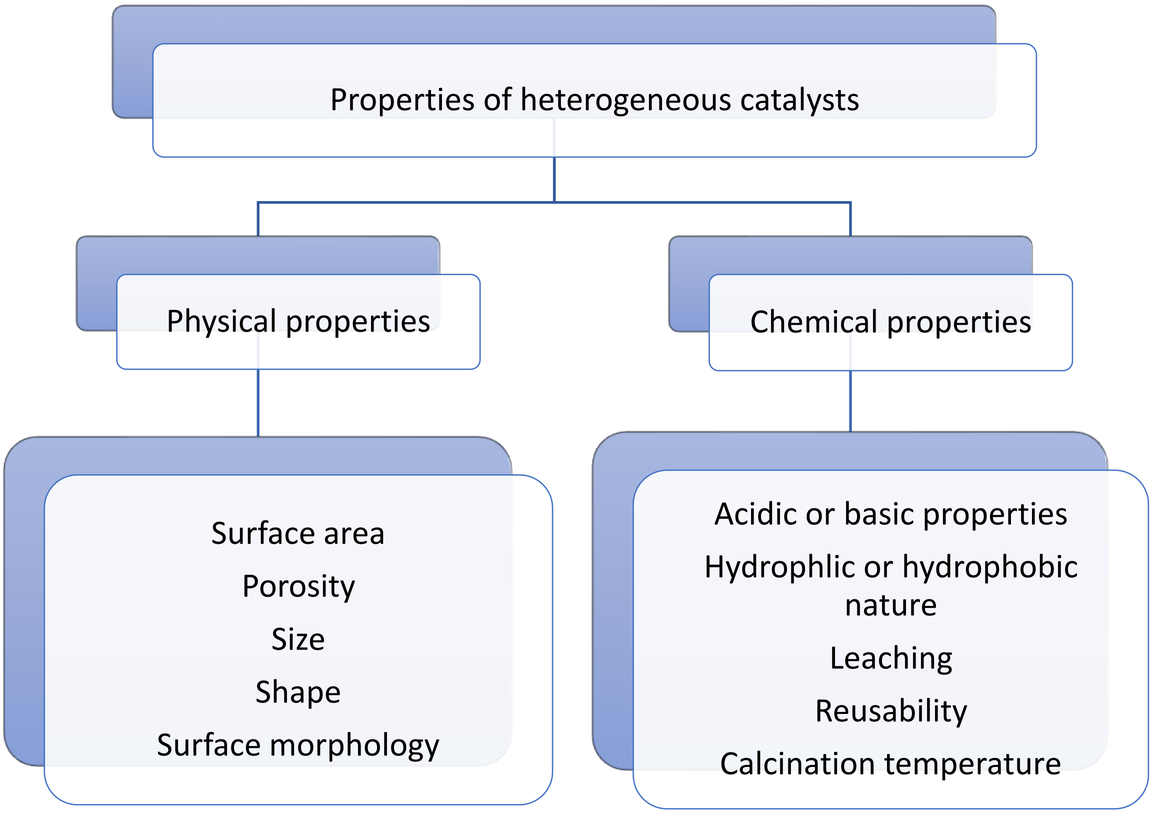


Figure 6. Heterogeneous catalyst properties for transesterification reaction [42].

Heterogeneous catalysts are gathered into acid and base catalysts. Acid catalyst has the advantage that they can be utilized for both concurrent esterification and transesterification process. Base catalyst requires lesser amount of the catalyst for the transesterification reaction to proceed. The main disadvantages reported for heterogeneous catalysts is, they tend to form three phases with oil and alcohol leading to mass transfer limitations with decreased rate of reaction [44]

2.5.3.1 Solid acid catalysts

Exploration of heterogeneous catalyst is vigorous due to various constrains during the production of biodiesel from homogeneous catalysts. Heteropoly acids and their derivatives were reported to be efficient heterogeneous catalyst for the transesterification reaction as they are tolerant to water. Heterogeneous catalysts are reported to be useful as they contain different strengths of Lewis acidity. Heterogeneous acid catalyst such as sulphated zirconia and tungstated zirconica are detailed for the conversion of triglycerides to fatty acid methyl esters for better yield than homogeneous catalyst. Biodiesel yield by homogeneous catalyst was compared with heterogeneous catalyst such as

WO_X/Al_2O_3(WAL), WO_X/SiO_2/ ZnO and WOx/SnO_2. The activity showed to be better with SiO_2 followed by ZnO with the yield of 98% under optimum conditions of 0.3 wt% methanol to oil, 10 g of catalyst, reaction temperature of 110 °C and 2 h of reaction time. Thus, the mass transfer limitations in the liquid phase reactions can be solved by using catalyst support such as zinc, zirconium and silica [44].

2.5.3.2 Solid base catalysts

Solid base catalyst is widely favored on account of its activity and strong basic sites. Base solid catalysts such as single metal, blended metal, doped metal oxides, alkali earthmetals and transition metal oxides are widely used. The basic sites of metal oxides are generated from metal ion which contains Lewis acid and the Brønsted base site from anion. The MgO, CaO, SrO, BaO are the various single metal oxides cited for base catalyzed transesterification reaction. The quality of MgO as base solid catalyst ispowerless and less dissolvable in alcohol. The strength of MgO catalyst increases with increasing the calcinating temperature to 600 °C.

The solid catalyst Zno-La_2O_3 is utilized for the production of biodiesel with a yield of 92.3% under batch reactors [44]. This catalyst appeared way better movement to 17 times through recycling nature. The CaO is reported to be more dynamic than MgO due to their strong basic site of catalyst. Alkaline earth metal oxides are proved to effective for low fatty acids at mild operating conditions. In order to increase the stability and activity, researchers focused on the doped metal oxides as solid catalyst. Doping of alkali tends to improve the surface area, strength and pore size of the synthesized material. The activity of Li-doped was reported to be effective with 23 wt% of doping with CaO. The yield was found to be closer to 100% with 20 min of reaction time [44].

A base catalyst in the heterogeneous form aims to overcome the limitations related with the utilization of homogeneous base catalyst, including the saponification that hinders the separation of glycerol from methyl ester layer. Other than, it moreover shows high catalytic activity within the transesterification process under mild conditions [45].

2.5.3.3 Layered double hydroxide (LDH)

Layered double hydroxide (LDH) is a mixed-metal hydroxide clay that consists of octahedral double hydroxyl layers with high positive charges, negatively charged interlayers and water molecules [46]. LDH has some advantages such as its low cost, non-toxicity, simplicity, higher adsorption capacity, and has a high thermal stability [47].

Due to their prospective applications over the past two decades, LDHs have drawn increasing attention [48–49]. In addition, LDH materials and their mixed metal oxides and solid solution after calcination were widely researched in the field of environmentally friendly reactions and catalysts [50–51] due to their distinctive characteristic. As is well established, LDHs have been synthesized using a range of techniques that heavily link the existence of feasible activity sites to the preparation approach [52-53].

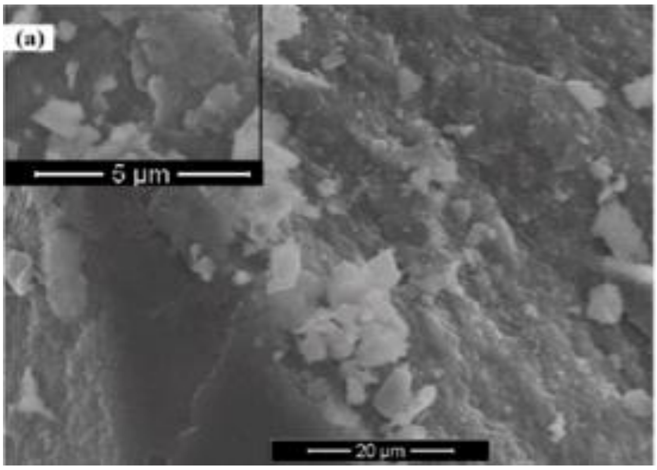


Figure 7. SEM images (a) MgAl-HDL [54].

Table 6. Summary of various heterogeneous catalysts used in the transesterification reaction of waste cooking oil.

Catalyst	**Time(min)**	**Temperature(°C)**	**Catalyst loading (wt%)**	**Methanol: Oil ratio**	**Yield (%)**	**Reference**
CaO	120	65	0.78	12:1	≥ 99 (soap Formation occurred)	[55]
Oil Palm Ash (K_2O major component)	30	60	5.35	18:1	71.74	[56]
CaO	180	60	2	7:1	≥ 80.0	[57]
CaO-La_2O_3	180	58	5	20:1	~ 96.0	[58]
Mg-Al hydrotalcite	360	120	6	24:1	≥ 90	[59]
Mg-Al hydrotalcite or Mg-MCM-41	300	60	0.5	65 mL methanol and 5 g oil	97 or 87	[60]
ZnO-La_2O_3	180	200	3	180:126 (wt/wt)	96	[61]
K_3PO_4 (tri-potassium phosphate)	120	60	4	6:1	97.3	[62]
$Al(HSO_4)_3$	50	220	0.5	16:1	81	[63]
Heterogeneous base catalyst						
Na-Mg-Al hydrotalcite (HT-Na)	480	60	7	9:1	67	[64]
CaO-ZrO_2	120	65	10	30:1	92	[65]
KOH/Al_2O_3	120	70	5	9:1	96.8	[66]

The catalysts mentioned in Table 6, show good catalytic activity in biodiesel production from low cost waste cooking oil feedstocks. However, several problems such as separation, recycling, soap formation, leaching, reactor corrosion, etc., are associated with these catalysts while using for biodiesel production from low cost feedstocks containing high free fatty acids and water contents.

3. TECHNICAL DESCRIPTION AND PROCEDURES

3.1 CHEMICALS AND RAW MATERIALS

For the transesterification reaction with choline hydroxide, the IL was purchased from Sigma Aldrich, methanol from Riedel-de-Haën, and sunflower oil, used as raw material, is from a commercial brand sold in portuguese markets. Oleic acid, tech 90%, was from ThermoFischer. Ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate, $BMIMHSO_4$, was obtained from Sigma Aldrich. For the characterization and analysis of biodiesel produced several reagents were used: n-heptane (99%) and sodium sulfate anhydrous purchased from Carlo Erba, hydrochloric acid was purchased from Honeywell, diethyl ether, borax, and red methyl indicator were obtained by Riedel-de-Haën. 37 FAME mixture, and boron trifluoride-methanol solution were purchased from Sigma Aldrich. The methyl heptadecanoate (97%) was obtained by Tokyo Chemical. Phenolphthalein indicator (99%), and sodium chloride were obtained by Panreac.

3.2 EQUIPMENT

For biodiesel synthesis, an automatic heating plate model C-MAG HP4, from IKA, using a condenser to reflux the excess of methanol from the reaction solution was used. For phase separation of the transesterification reaction product, a centrifuge (SIGMA, model 2-4) was utilized, and for drying the phases, an oven (SCIENTIFIC, series 9000) was used. The samples masses were measured with an analytical balance with a precision of ±0.0002 g (AE, model ADA 210/C). A gas chromatography system (SHIMADZU Nexis GC-2030) equipped with an FID detector, an autoinjector AOC- 20i, and an OPTIMA BioDiesel F (30mx0.25mmx0.23µm) capillary column was also used to determine the FAMEs content in biodiesel samples.

3.3 METHODOLOGY

3.3.1 Transesterification Reaction of Sunflower Oil

In a 100 mL two necked reaction flask, the necessary amount of sunflower oil was taken in. The ionic liquid was weighed, and methanol was heated and also added into it. The reaction flask was subsequently immersed in a paraffin bath (1) coupled with a reflux condenser (2) and positioned over an automatic agitation heating plate (3) with automatic temperature control. The mixture was heated to the desired temperature and the reaction time count was initiated after that. As shown in Figure 8, an extra thermometer (4) was used to validate the temperature inside the reaction flask.

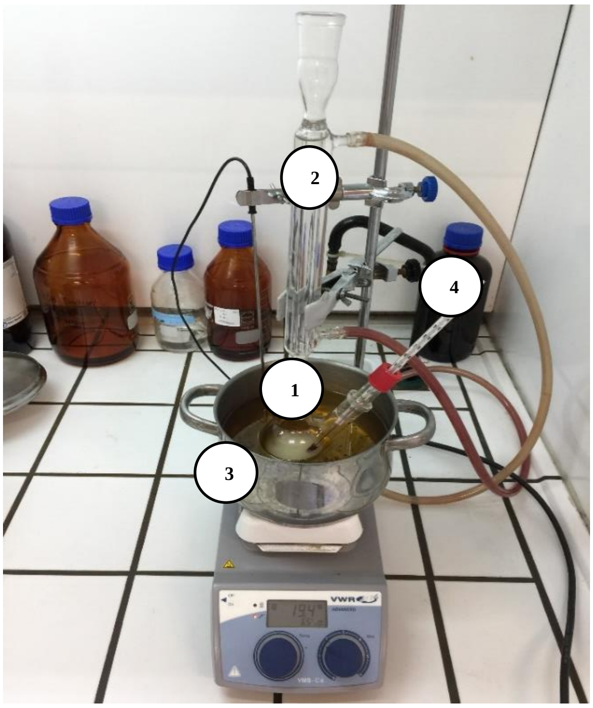


Figure 8. Experimental apparatus for the transesterification reaction.

The stirring was stopped at the end of every reaction time, and the resultant mixture was set aside to cool in cold water to stop the reaction. After that, the mixture was transferred into a separating funnel for phase separation for 15 hours. After this period, each phase was transferred to centrifuge tubes and subjected to 30 minutes of centrifugation (3000 rpm). Complete separation of the phases was reached, and Pasteur pipettes were used to separate the phases. After that, the samples were dried in an oven at 110 °C for approximately 28 h, then stored in the fridge until the moment of analysis. The appearance of the two phases that form after separation can be seen in Figure 9.

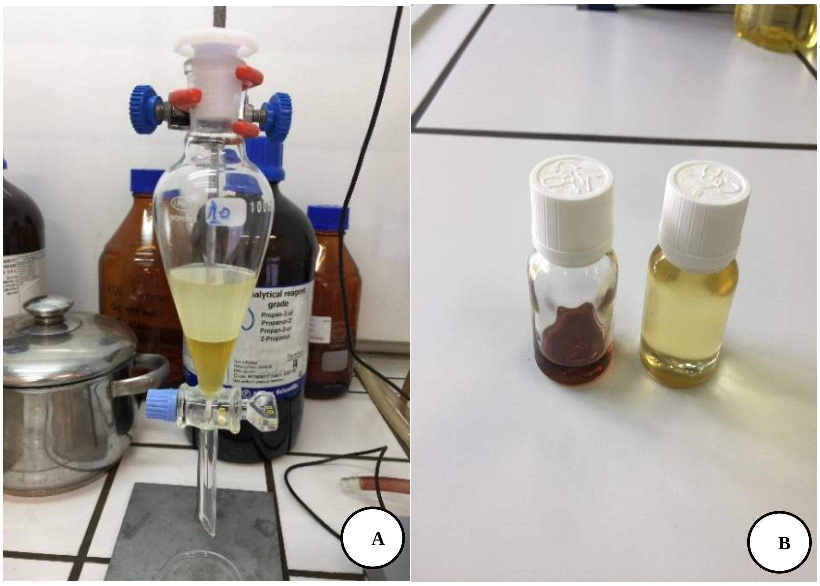


Figure 9. **A**: Phase separation obtained after the reaction: the upper phase is FAMEs, and the lower phase is the mixture of unreacted methanol, glycerol, and catalyst. **B**: Flasks with separated phases after drying: lower phase (left flask) and upper phase (right flask).

3.3.2 Acidity Measurement

The acidity value was determined to assess the amount of free fatty acids (FFAs) in the oil used as raw material used in the produced biodiesel. The measurement was carried out in accordance with EN 14104:2003 Standard [67]. Initially, 0.5 grams of oil sample was transferred to an Erlenmeyer using a micropipette, and an analytical balance was used to measure the weight. After this, 12.5 mL of the solvent ethanol/diethyl ether 1:1 (v/v) and 5 drops of phenolphthalein were added into the flask. Then, the solution was titrated with a standard alcoholic solution of potassium hydroxide. The acid value is given in terms of mg of KOH/g sample according to Equation 1.

$$AV = \frac{VKOH*CKOH*MWKOH}{m_{biodiesel}} \tag{1}$$

In this equation, V_{KOH} is the volume, in mL, of the KOH solution used in the titration, C_{KOH} is the concentration of the KOH solution, in mol. L^{-1}, MW_{KOH} is the KOH molecular weight, which is 56.1 g.mol^{-1}, and m_{Sample} is the oil masses samples measured, in g.

3.4 CHARACTERIZATION OF BIODIESEL

3.4.1 FAME content by gas chromatography

The fatty acid methyl ester (FAME) content of the produced biodiesel was characterized by gas chromatography (GC) analysis in compliance with the European Standard EN14103:2003 [68]. This analytical technique provides the distribution area corresponding to each component present in the sample. Figure 10 shows the equipment used to perform these analyses.

Figure 10. GC-FID equipment used for FAME content analysis in biodiesel sample.

For the sample preparation, 250 mg aliquots of the biodiesel produced were transferred to 15 mL flasks, and 5 mL of methyl heptadecanoate solution prepared with heptane with a concentration of 5 mg. mL^{-1}, and used as internal standard, was added with a micropipette. A small amount of anhydrous sodium sulfate was added to remove any remaining moisture in the samples. Then, the solution was agitated and left to stand for at least 1 min, and a sample volume of 1 mL was transferred to a 2 mL GC vial in order to perform the GC analysis.

The operating conditions used in every GC analysis were based on a helium flow of 1 mL. min^{-1}, an oven temperature program which started with a temperature of 50 °C, maintained for 1 min and followed by an increase in temperature up to 200 °C at a rate of 25 °C/min. Then, it was once again increased to 230 °C with a heating rate of 3 °C/min, maintained for 3 minutes. The final temperature was maintained for 23 min, for a total running time of 40 min. The injector was operated at 250 °C. The injector was used in split mode, with a split ratio of 1:100, and the detector temperature was 250 °C, and the injected sample volume was 1 μL.

The identification of each methyl ester present in the sample was performed by the comparison with the retention time of the FAME compound mixture analysis obtained in this work with the GC Shimadzu system under the operational conditions mentioned above with the retention times obtained in other analyzes made available by manufacturers. One of them is the chromatogram obtained from one 37 FAME compound mixture supplied by Supelco using an Omegawax ™ 250 column, shown in Figure 11 [68]. The other one is the chromatogram of a 16 FAME mix analysis published by Macherey-Nagel using column OPTIMA BioDiesel F obtained with the same stationary phase but with a different temperature program [69]. The chromatogram obtained from the 37 FAME compound mixture in this work is presented in Figure 12.

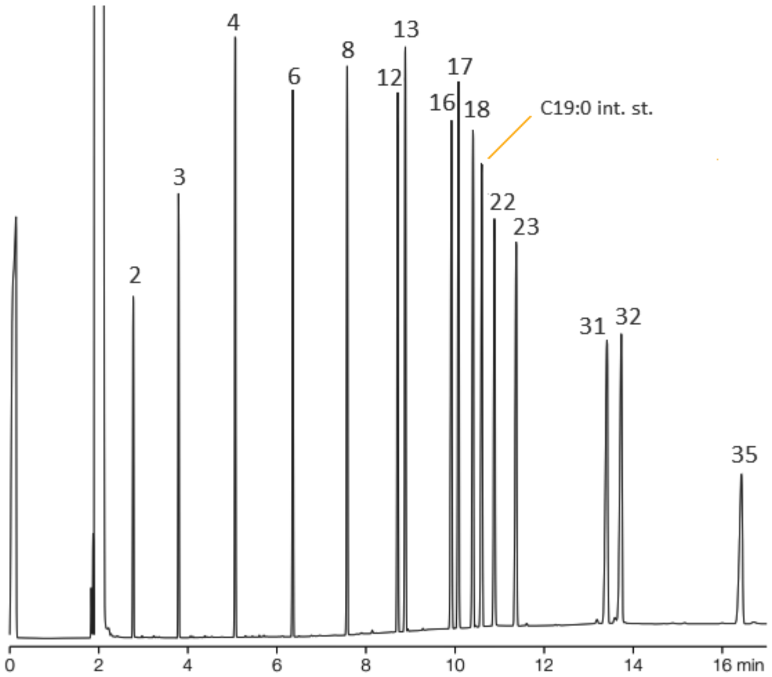


Figure 11. Chromatographic analysis obtained for the Supelco 37 Component FAME Mix on the Omegawax 250 column.

Source: Adapted from Supelco [68].

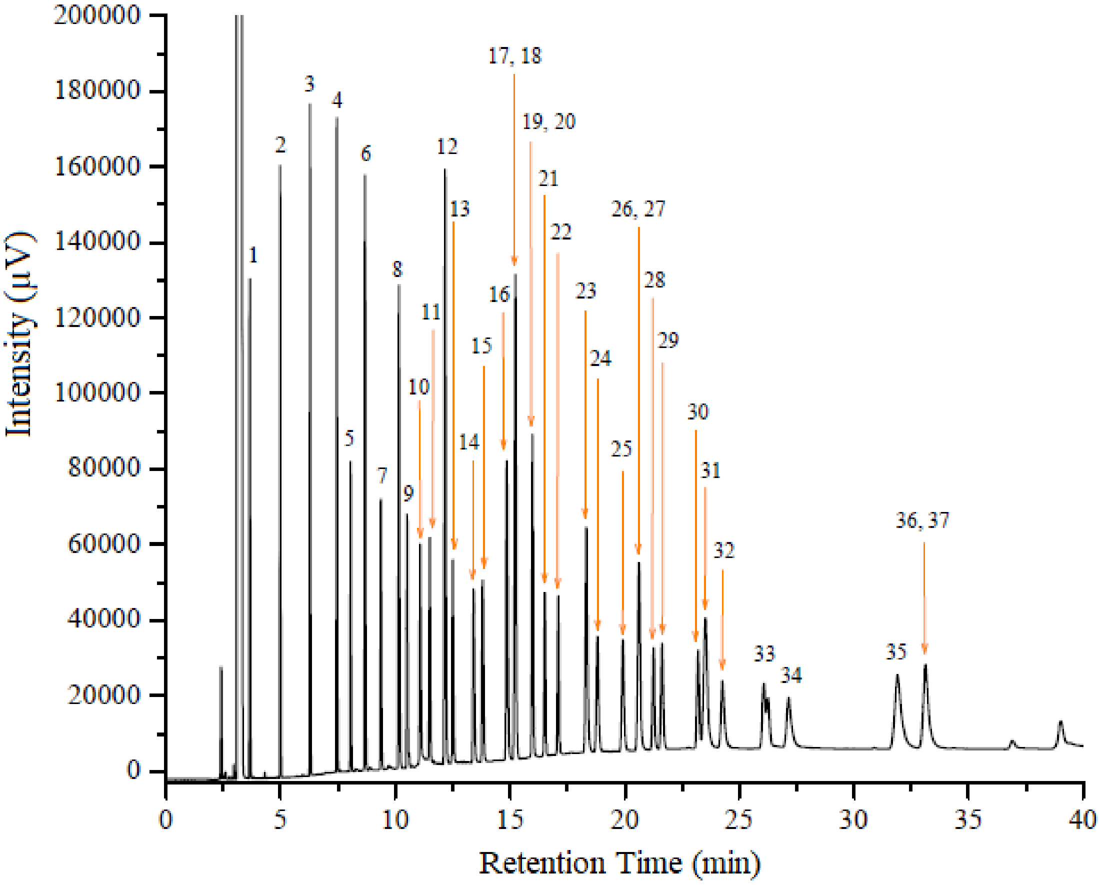


Figure 12. Chromatographic analysis obtained for the 37 compound FAME mix using the Shimadzu equipment with an OPTIMA BioDiesel F column.

Table 7 shows the elution order, compound name, compound ID, retention time and the obtained chromatographic area, for the analysis of the Supelco 37 compound FAME mix used in this work and presented in Figure 12. This table is used to identify each FAME peak in the analysed samples. These peaks are subsequently selected for the estimation of the individual FAME contents, and the total FAMEs content, in the biodiesel samples. The percentage of FAME content was calculated using Equation 2.

$$C(\%) = \frac{(\sum A_{FAME} - A_{IS})}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m_{biodiesel}} \times 100 \qquad (2)$$

Where $\sum A_{FAMEs}$ is the total peak area of all methyl esters from C4:0 to C22:0 provided by the chromatograph, as shown in Table 7. A_{IS} is the peak area corresponding to methyl heptadecanoate, used as internal standard, C_{IS} is the concentration, in milligrams per milliliter, of the methyl heptadecanoate solution, V_{IS} is the volume, in milliliters, of the methyl heptadecanoate solution, and $m_{biodiesel}$ is the mass, in milligrams, of the biodiesel sample.

Table 7. Elution order, compound name, compound ID and retention time for the 37 compounds.

Elution Order	**Compound Name**	**Compound ID**	**Retention Time (min)**	**Area (μV)**
1	Butyric acid methyl ester	C4:0	3.662	237909
2	Caproic acid methyl ester	C6:0	4.989	300934
3	Caprylic acid methyl ester	C8:0	6.285	346056
4	Capric acid methyl ester	C10:0	7.459	373026
5	Undecanoic acid methyl ester	C11:0	8.053	189411
6	Lauric acid methyl ester	C12:0	8.686	391380
7	Tridecanoic acid methyl ester	C13:0	9.376	195725
8	Myristic acid methyl ester	C14:0	10.171	396472
9	Myristoleic acid methyl ester	C14:1	10.517	202181
10	Pentadecanoic acid methyl ester	C15:0	11.085	240538
11	cis-10-Pentadecanoic acid methyl ester	C15:1	11.498	225487
12	Palmitic acid methyl ester	C16:0	12.172	618875
13	Palmitoleic acid methyl ester	C16:1	12.514	205280
14	Heptadecanoic acid methyl ester	C17:0	13.413	203369
15	cis-10-Heptadecanoic acid methyl ester	C17:1	13.819	199608
16	Stearic acid methyl ester	C18:0	14.872	404805
17, 18	Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	15.232	606043
19, 20	Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	15.987	398602
21	gamma-Linolenic acid methyl ester	C18:3n6	16.521	192867
22	Linolenic acid methyl ester	C18:3n3	17.106	184840
23	Arachidic acid methyl ester	C20:0	18.341	411741
24	cis-11-Eicosenoic acid methyl ester	C20:1	18.811	205112
25	cis-11,14-Eicosadienoic acid methyl ester	C20:2	19.918	201257
26, 27	cis-8,11,14-Eicosatrienoic acid methyl ester, Heneicosanoic acid methyl ester	C20:3n6, C21:0	20.620	399305
28	cis-11,14,17-Eicosatrienoic acid methyl ester	C20:3n3	21.257	182797
29	Arachidonic acid methyl ester	C20:4n6	21.629	194860
30	cis-5,8,11,14,17-Eicosapentaenoic acid methyl ester	C20:5n3	23.212	183432
31	Behenic acid methyl ester	C22:0	23.524	412668
32	Erucic acid methyl ester	C22:1	24.264	202911
33	cis-13,16-Docosadienoic acid methyl ester	C22:2	26.076	172304
34	Tricosanoic acid methyl ester	C23:0	27.149	204729
35	Lignoceric acid methyl ester	C24:0	31.893	414423
36, 37	cis-4,7,10,13,16,19-Docosahexanoic acid methyl ester, Nervonic acid methyl ester	C22:6n3, C24:1	33.116	377957

3.4.1.1 Preparation of methyl heptadecanoate solution

The internal standard method was performed to quantify the FAME content (wt.%) present in the biodiesel samples produced. To prepare the solution, 250 mg of methyl heptadecanoate was measured and transferred to a volumetric flask of 50 mL. Then n-heptane was used to fill the remaining volume in order to reach a final concentration of 5 mg.mL^{-1}.

3.4.1.2 Derivatization of fatty acids by BF_3

The derivatization procedure of the methyl esters of fatty acids by boron trifluoride (BF_3) was performed to determine the distribution of the fatty acids present in the feedstock used in the production of biodiesel and decrease the potential damage to the column and/or instrument [70]. This process consists of the transformation of the triacylglycerols, and fatty acids present in the sample feedstock into methyl esters, followed by the quantification of compounds between Myristic acid methyl ester (C_{14}) and Lignoceric acid methyl ester (C_{24}) by gas chromatography.

Initially, the necessary solutions of methanolic KOH and methyl heptadecanoate were prepared. The methanolic KOH solution was prepared by adding the proper amount of potassium hydroxide in methanol to make a 0.5 mol. L^{-1} solution. Thus, 25 mg of the feedstock sample and 2.5 mL of the methanolic solution of KOH (0.5 mol. L^{-1}) were added to a 20 mL flask. Then, the flask was closed and submitted to a drying process in an oven at 90 °C for 10 min, thereafter, it was removed from the oven and waited to cool to room temperature. After, 2 mL of BF_3 in methanol solution (10% v/v) was added in the flask, and it was closed and placed in the oven at 90 °C for more 30 min. Again, it was removed from the oven and allowed to cool to room temperature. After that, 3 mL of methyl heptadecanoate solution was added into the flask, and it was agitated using a vortex apparatus. Then, 2 mL of saturated sodium chloride solution was added and the solution was subjected once again to the vortex agitation. The sample was centrifuged for 5 min at 3000 rpm for the separation of the two phases. By the end, 2 mLof the upper phase was reserved into a 4 mL flask. A small amount of anhydrous sodium sulfate was added to remove all moisture present before gas chromatography analysis was performed.

3.5 KINETIC STUDY

The experimental dosage of catalyst was selected to evaluate the reaction kinetics. Regarding temperature and alcohol/oil molar ratio reaction parameters, their selection was made based on an analysis of what had been reported in the literature so far about the kinetic study with the choline hydroxide catalyst.

Therefore, a kinetic modelling study on ChOH was performed under the specific conditions of 2% catalyst dosage, 10:1 alcohol/oil molar ratio, for the periods of 10, 20, 30, 45, 60, and 120 minutes for the temperature of 65, 55, 45 and 35 ℃ [17].

The procedure for the reaction was similar to the one presented in Section 4.3.1. In order to guarantee an efficient reaction mixture, a uniform distribution of the catalyst, and also, to avoid the possibility of modification of the contents inside the reaction flask with sample removal due to a reaction execution with small amounts of reagents, it was decided to carry out a reaction for each defined planning time.

3.6 ACTIVATION OF LDHs BY INTERCALATION OF IONIC LIQUID

3.6.1 Protocol

Due to their structural merits that arise from their stability and high surface area, the layered double hydroxide (LDH) materials have caused strong attention.

The Layered Double Hydroxide (LDH) Mg-Al-CO_3 used in this work was synthesized by Professor Mehdi Adjdir, in Algeria. All experiments were carried out at 25 °C in a thermostatic bath. A different mass of solid LDH was mixed with 10 mL of aqueous solution containing 1-butyl-3-methylimidazolium hydrogen sulfate, BMIM HSO_4, ionic liquid for 48 h at different concentrations from 108 to 50 ppm separately. The activation of LDHs by intercalation was made with 0 (blank test), 1, 2, 4 and 5 wt% of IL (Table 8). After this procedure phases separation was performed with a high-speed centrifuge at a rate of 8000 rpm and the solid was dried in an oven for 30 min at 90°C.

Table 8. Data for esterification reaction using LDH.

Exp	% IL	m LDH (mg)	m IL (mg)	m AO (mg)	MeOH (mL) (1/60)
1	0	51.4	0	9.1	0.86
2	1	50.0	0.6	7.1	0.43
3	2	52.5	1.4	10.4	0.86
4	4	49.7	2.0	22.5	1.72
5	5	50.8	2.8	25.2	2.15
6	1	99.9	1.6	9.8	0.86

3.6.2 Esterification reaction

For the performance evaluation of this catalyst concerning biodiesel production, some preliminary studies were conducted using oleic acid (OA) as raw material. The dosage of catalyst was 10% related to OA mass and a ratio OA/MeOH of 1/60 was used (Table 8).

The esterification reaction was carried in a shaking incubator for 24 hours at 50 °C. When the pre- determined reaction time was achieved, the tubes were removed from the shaking incubator and waited to cool to room temperature. After 2 mL of methyl heptadecanoate solution were added in the solution, the samples were centrifuged for 10 min at 3000 rpm for the separation of the two phases. By the end, 2 mLof the upper phase was reserved into a 4 mL flask, then the gas chromatography analysis was performed.

4. RESULTS AND DISCUSSION

4.1 FEEDSTOCK CHARACTERIZATION

Sunflower oil (SFO) was analysed by gas chromatography to determine the distribution of fatty acids, as described in Section 4.4.1. The fatty acids were identified by comparison with fatty acid methyl esters and the substances retention time of the 37 FAME mixture. GC analysis showed that, monounsaturated oleic acid (C18:1), and polyunsaturated linoleic acid (C18:2) were the major chemical components, with 26.9 and 60.0%, respectively, saturated palmitic acid (C16:0) and stearic acid (C18:0) also appear in smaller quantities, as can be seen in Table 9 for SFO.

Table 9. Percentage of fatty acids identified as methyl esters of triacylglycerols in sunflower oil.

Compound Name	**Compound ID**	**%FAME**		**Average (%)**
		Sample 1	**Sample 2**	
Palmitic acid	C16:0	6.40	6.50	6.45
Stearic acid	C18:0	3.70	3.90	3.80
Oleic acid, Elaidic acid	C18:1 (c+t)	27.00	26.70	26.85
Linoleic acid, Linolelaidic acid	C18:2 (c+t)	59.80	60.10	59.95
Total		**96.90**	**97.20**	**97.05**

Figure 13 shows the GC-FID chromatogram obtained after the derivatization of sunflower oil.

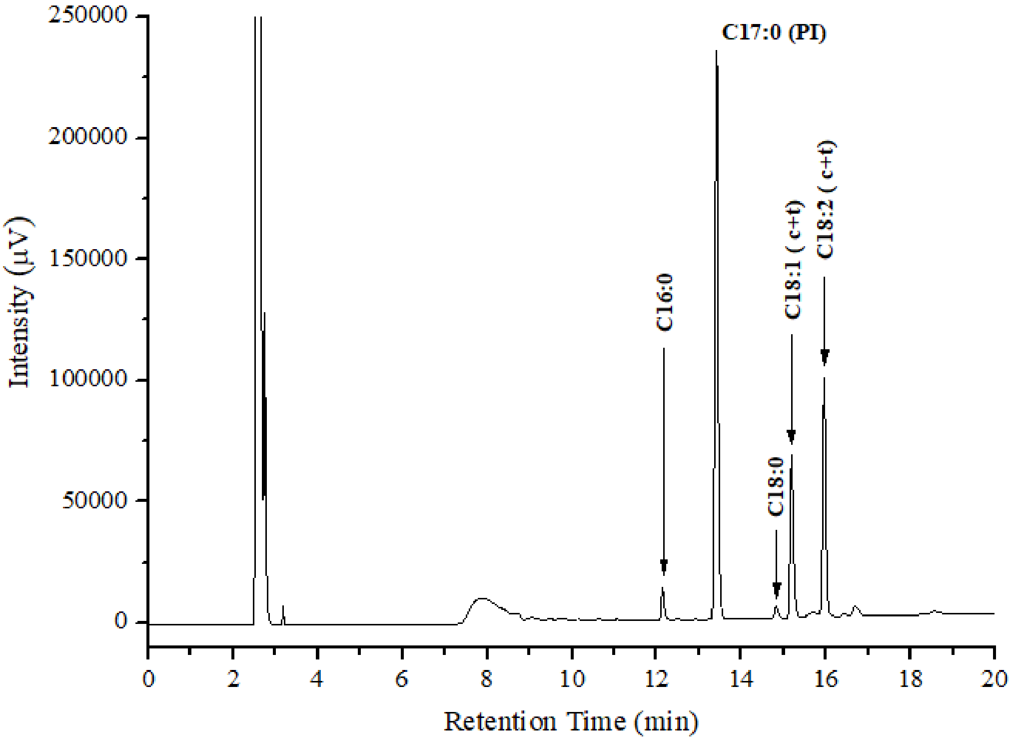


Figure 13. Chromatogram obtained after the derivatization of sunflower oil [17].

The acidity value (AV) for samples of feedstock was determined in triplicate, and the results are presented in Table 10. The acidity value found for the sunflower oil was very low (0.46 mg KOH/g oil).

Table 10. Acidity value data obtained for the raw material.

Oil Sample	**Mass (g)**	**VKOH (mL)**	**CKOH (mol. L^{-1})**	**AV (mgKOH.g^{-1})**	**AV Average (mgKOH.g^{-1})**
SFO	0.4991	0.040	0.08799	0.396	0.458
	0.5009	0.060	0.08799	0.591	
	0.5111	0.040	0.08799	0.386	

*Measurements done with micropipettes of 20 µL.

4.2 KINETIC STUDY

Choline hydroxide was selected as ionic liquid. ChOH was purchased in a 45 wt.% methanol solution, so to confirm the concentration of the IL solution for the transesterification reactions, an acid-base titration was performed. It was found out that the mass percentage of ChOH in the solution was 36.9%.

By the comparison of the ChOH catalytic activity in the transesterification reaction, a higher yield in esters was achieved with 2% concentration of catalyst. Therefore, it was selected for the following experiments.

The transesterification reactions were performed with sunflower oil and methanol using a catalyst dosage of 2%, and 1:10 oil/MeOH molar ratio, for the periods of 10, 20, 30, 45, 60, and 120 minutes and temperature of 65, 55, 45, and 35°C. The obtained results are shown on Figure 14.

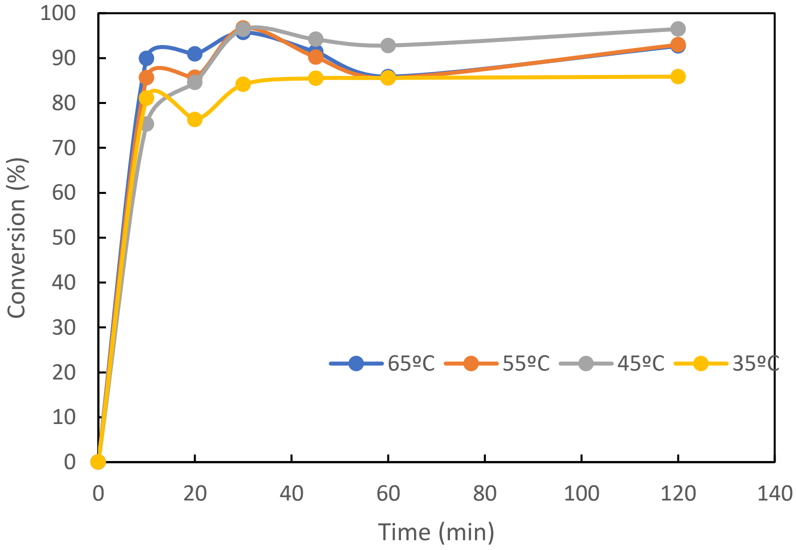


Figure 14. Conversion versus time for transesterification reaction at different temperatures.

It can be seen from Figure 14 that after 30 minutes of reaction the conversion is almost constant, meaning that this time is enough for the reaction to occur.

Figure 15 shows the chromatogram obtained for biodiesel produced after 60 minutes of reaction at 65°C and is an example of the chromatograms obtained for all reaction experiments. The main peaks present refer to palmitic acid methyl ester (1), heptadecanoic acid methyl ester (2), stearic acid methyl ester (3), oleic acid methyl ester, elaidic acid methyl ester (4) and linoleic acid methyl ester, linolelaidic acid methyl ester

(5).

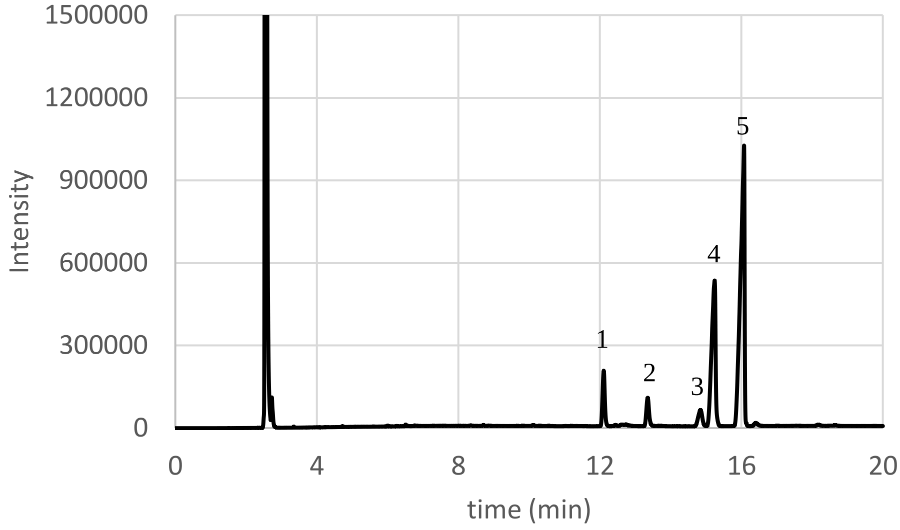


Figure 15. Chromatogram for biodiesel produced at 65°C, after 60 min of reaction.

As indicated in Section 1.4.2, the transesterification reaction occurs in three continuous reversible processes, in which, first, triacylglycerol (TAG) reacts with methanol to produce diacylglycerols (DAG), then reacts with methanol to yield diacylglycerols (MAG) that further reacts with methanol to produce methyl ester (ME) and glycerol (GL). Therefore, six rate constants are reported in the literature for the whole reaction from TAG to methyl ester, as shown by Equations 3, 4, and 5.

$$TAG + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} DAG + R^{\prime}CO_2R \tag{3}$$

$$DAG + ROH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} MAG + R^{\prime}CO_2R \tag{4}$$

$$MAG + ROH \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} GL + R^{\prime}CO_2R \tag{5}$$

Since transesterification reactions with methanol result ultimately in the production of methyl esters, the intermediate reaction products can be neglected, and a simple mathematical model that expresses the overall conversion as a single-step reaction can then be considered (see Equation 6) [71, 72, 73], and the reaction rate can be described by Equation 7. Thus, the following assumptions were made aiming to simplify the kinetic model: i) Change in concentration of catalyst and the possibility of reverse reaction are ignored by using a sufficient quantity of catalyst; ii) Reaction mixture and catalyst are distributed uniformly; iii) Methanol concentration is considered constant during the reaction; iv) Intermediate reagents produced during reactions were neglected.

$$TAG + 3ROH \xrightarrow{Catalyst} 3R^{\prime}CO_2R + \ GL \tag{6}$$

$$-r = -\frac{d[TAG]}{dt} = \ k[TAG]^a \tag{7}$$

Where k is the rate constant for the reaction, $[TAG]$ is the triacylglycerol's concentration, and t is the reaction time (min).

Due to the fact that the data obtained were in terms of methyl esters yield, Equation 7 was combined with Equation 8 to determine the order of the reaction by applying the integral method, with a equal to 0, 1, 2, and 3, giving origin to Equations 9- 12, respectively.

$$[TAG] = [TAG]_0(1 - X) \tag{8}$$

$$\mathrm{x} = \frac{\mathrm{k}}{[\mathrm{TAG}]_0}\mathrm{t} \tag{9}$$

$$-ln\,(1 - X) = k\ \mathrm{t} \tag{10}$$

$$\frac{\mathrm{X}}{1-\mathrm{X}} = \mathrm{k}[\mathrm{TAG}]_0\mathrm{t} \tag{11}$$

$$\frac{1}{2(1-X)^2} = \frac{1}{2} + k[TAG]_0^2t \tag{12}$$

where $[TAG]_0$ is the initial triacylglycerol concentration, and X is the conversion in FAME (%).

Tables 11, 12, 13, and 14 summarize the data obtained for each proposed reaction order, for the first 30 minutes of reaction.

Table 11. Data for each reaction order proposed at 65 °C.

Time (min)	Conversion	0 th Order X	1 st Order $-ln(1-X)$	2 nd Order $\frac{X}{1-X}$	3 rd Order $\frac{1}{2(1-X)^2}$
0	0.0000	0.0000	0.0000	0.0000	0.5000
10	0.8994	0.8994	2.2966	8.9403	49.4053
20	0.9091	0.9091	2.3979	10.0011	60.5121
30	0.9572	0.9572	3.1512	22.3644	272.9496

Table 12. Data for each reaction order proposed at 55 °C.

Time (min)	Conversion	0 th Order X	1 st Order $-ln(1-X)$	2 nd Order $\frac{X}{1-X}$	3 rd Order $\frac{1}{2(1-X)^2}$
0	0.0000	0.0000	0.0000	0.0000	0.5000
10	0.8562	0.8562	1.9393	5.9541	24.1797
20	0.8568	0.8568	1.9435	5.9832	24.3828
30	0.9668	0.9668	3.4052	29.1204	453.6217

Table 13. Data for each reaction order proposed at 45 °C.

Time (min)	Conversion	0 th Order X	1 st Order $-ln(1-X)$	2 nd Order $\frac{X}{1-X}$	3 rd Order $\frac{1}{2(1-X)^2}$
0	0.0000	0.0000	0.0000	0.0000	0.5000
10	0.7530	0.7530	1.3983	3.0485	8.1955
20	0.8457	0.8457	1.8688	5.4808	21.0009
30	0.9640	0.9640	3.3242	26.7777	385.8024

Table 14. Data for each reaction order proposed at 35 °C.

Time (min)	Conversion	0 th Order X	1 st Order $-ln(1-X)$	2 nd Order $\frac{X}{1-X}$	3 rd Order $\frac{1}{2(1-X)^2}$
0	0.0000	0.0000	0.0000	0.0000	0.5000
10	0.8994	0.8994	2.2966	8.9403	49.4053
20	0.9091	0.9091	2.3979	10.0011	60.5121
30	0.9572	0.9572	3.1512	22.3644	272.9496

In this approach, the rate constant *k* is obtained by plotting a graph of the extent of reaction versus time that gives a straight line if the hypothesis concerning the mathematical form of the rate expression is correct [74].

It turns out that most of the kinetic studies on transesterification that applied the simplification of the reaction rate expression found in the literature assume pseudo-first-order kinetics [71,72,73].

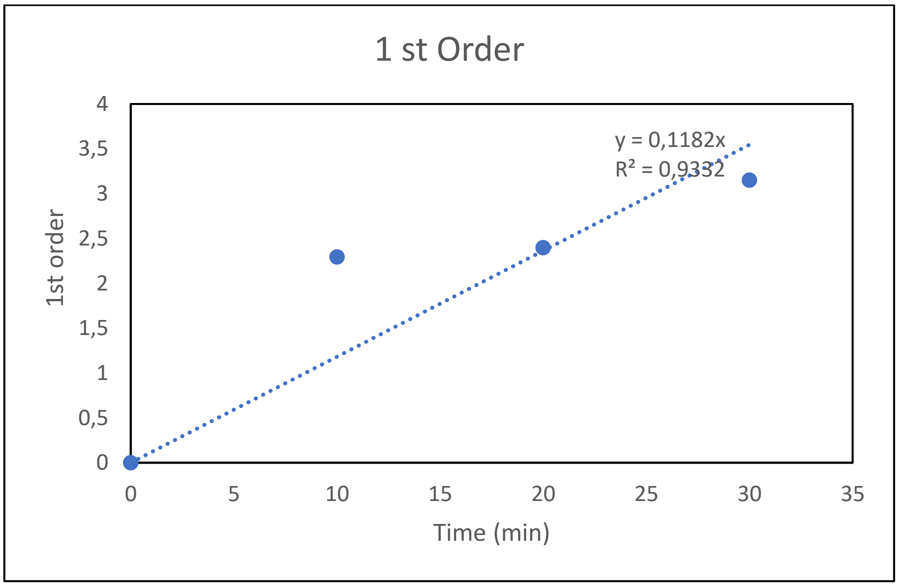


Figure 16. Fit of first order reaction for 65°C.

Table 15. values of the determination coefficient of the other reaction temperatures for the first order.

Temperature (°C)	R^2
55	0.9607
45	0.9883
35	0.8790

The coefficients of determination for each temperature and each trial are displayed on Table 16.

Table 16. Coefficient of determination obtained applying the integral method for several reaction orders.

	R^2			
Temperature (°C)	0th order	1st order	2nd order	3rd order
65	0.8745	0.9332	0.9686	0.8673
55	0.8899	0.9607	0.8613	0.7096
45	0.9198	0.9883	0.8405	0.6974
35	0.8665	0.8790	0.8909	0.8907

The integrated form of the reaction rate for a 1st order reaction is represented by equation (10). It is possible to retrieve a value of k'_1 for each temperature, which is appointed on Table 16. It can be seen that the constant value is almost the same for temperatures 45, 55 and 65°C and it is lower for 35°C.

Table 17. Kinetic constants for each temperature.

Temperature (°C)	k'_1 (min^{-1})
65	0.1182
55	0.1146
45	0.1079
35	0.0719

The kinetics constant k'_1 is related to the temperature by the Arrhenius equation, and it is given in the form of equation (13).

$$K'_1 = K_0 exp^{\frac{-Ea}{RT}} \qquad (13)$$

Where k'_1 is the kinetics constant at a determined temperature, k_0 is the pre- exponential factor, *Ea* is the activation energy, in kJ/mol, *R* is the gas constant, in kJ/(mol.K), and *T* is the temperature, in K. The Arrhenius equation establishes that at a given temperature *T*, the fraction of collisions between molecules with the minimum required energy Ea is proportional to exp(-Ea/RT) and therefore, the rate constant is also proportional to that same factor [75]. The Arrhenius equation can be linearized by applying the natural logarithm in both sides of equation (13), leading to equation (14).

$$\ln K'_1 = \ln k_0 - \frac{Ea}{RT} \qquad (14)$$

Therefore, by plotting the inverse of the temperature, in K, and the natural logarithm of the kinetics constant at each temperature, it is possible to estimate the activation energy for the reaction. The Arrhenius plot is displayed on Figure 20. A coefficient of determination of $R^2 = 0.7720$ was obtained, which is a low value. The pre-exponential factor (k_0) was estimated as 1.0266 min^{-1} and the activation energy (E_a) as 13.63 kJ/mol. The low activation energy indicates a certain temperature independency.

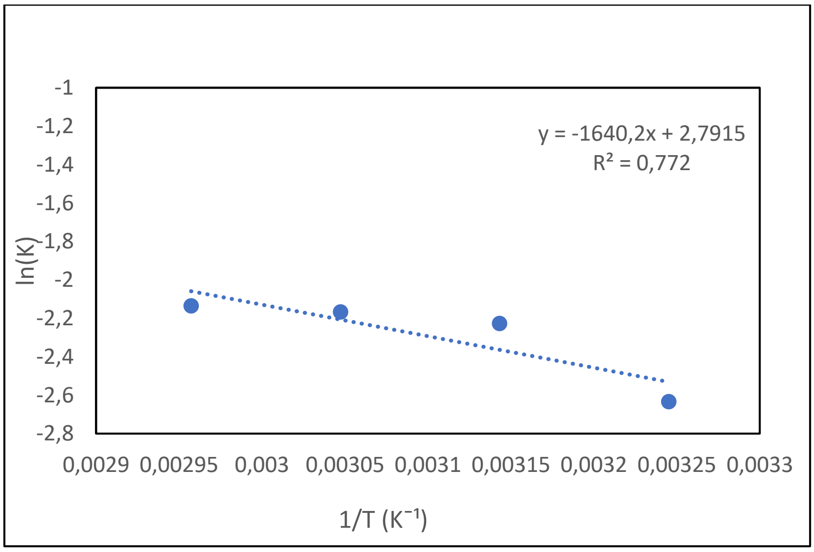


Figure 17. Estimation of the activation energy through the Arrhenius equation.

4.3 HETEROGENEOUS CATALYSTS

As mentioned in section 4.4.1 the percentage of FAME content was calculated using Equation 15.

$$C(\%) = \frac{(\sum A_{FAME} - A_{IS})}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{mOA} \times 100 \qquad (15)$$

Where $\sum A_{FAMEs}$ is the total peak area of all methyl esters from C4:0 to C22:0 provided by the chromatograph, as shown in Table 6. A_{IS} is the peak area corresponding to methyl heptadecanoate, used as internal standard, C_{IS} is the concentration, in milligrams per milliliter, of the methyl heptadecanoate solution, V_{IS} is the volume, in milliliters, of the methyl heptadecanoate solution, and mOA is the mass, in milligrams, of the oleic acid sample. According to the data of Table 8, 7 preliminary experiences were carried out with LDH and $BMIMHSO_4$. Experience 1 is the blank (without IL), and two experiences were done with the same percentage of IL (1%) but different mass of LDH. The results obtained in terms of FAME content are shown on Table 17.

Table 18. Conversion (%FAME) as a function of % IL.

% IL	Conversion %
0	3.8
1	3.4
2	3.7
4	1.3
5	1.6
1	0.6

The values presented on Table 17 seems to indicate that the activation of LDH by intercalation with BMIM HSO_4 was not successful, because the conversion values are very low. However, the result can be better if we try to improve the experimental methodology for the intercalation of LDH with ionic liquid, for example use other LDH or use other ionic liquid.

5. CONCLUSIONS

The main objective of this work was to study the application of an alkaline ionic liquid, choline hydroxide, as catalyst for biodiesel production using a vegetable oil and methanol as reagents and also to study the performance of a heterogeneous catalyst LDH activated by intercalation with $BMIMHSO_4$ IL for the esterification of oleic acid.

A kinetic study was carried out for the transesterification of a previously characterized vegetable oil sample, with methanol, using ChOH as catalyst, under the specific conditions: 2 wt.% catalyst dosage, 1:10 oil/methanol molar ratio, for the reaction times of 10, 20, 30, 45, 60 and 120 minutes at 35, 45, 55, and 65 ℃. The vegetable oil is composed essentially by palmitic acid methyl ester, heptadecanoic acid methyl ester, stearic acid methyl ester, oleic acid methyl ester, elaidic acid methyl ester and linoleic acid methyl ester, linolelaidic acid methyl ester. Transesterification with ChOH provided a 95.7% conversion in FAME content for 30 min of reaction at 65 ℃. The results of the kinetic study demonstrated that the first-order model was generally the best fit for the reaction kinetics considering all the temperatures, with a rate constant (k) estimated as 0.1182 min^{-1} for 65 ℃, and an estimated activation energy of 13.64 kJ/mol.

Our results are in accordance with the results of the transesterification reaction obtained by Ullah *et al*. (2017) which they demonstrated the reaction as a first order, and they estimated an activation energy of 19.24 kJ/mol [39].

The results obtained in this work are considered relevant for the application of basic ionic liquids in the catalysis of transesterification reactions of mixtures of triacylglycerols derived from sunflower oil with high FFA contents since ChOH revealed an excellent capacity for fast transesterification.

The activation of LDH by intercalation with BMIM HSO_4 was not successful, because the conversion values are very low.

5.1 SUGGESTIONS FOR FUTURE WORKS

In order to achieve a better conclusion on the applicability of ChOH ionic liquid in the production of biodiesel, it will be necessary to carry out further studies using the mentioned ionic liquid. Some suggestions for future work are:

(i) Evaluate the quality of the biodiesel produced, determining its properties, e.g. density, kinematic viscosity, water and ash content;

(ii) Apply the recovery process tested in the study of the number of cycles that ChOH can perform without significant loss of reaction yield.

Regarding the application of heterogeneous catalysts for the esterification reaction, in particular the use of LDH with an IL:

(iii) Improve the experimental methodology for the intercalation of LDH with ionic liquid, use other LDH or use other ionic liquid;

(iv) Apply another type of heterogeneous catalysts in transesterification and esterification reactions.

References

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APPENDIX A - Titration data of ChOH (CH_3OH) solution and Kinetic study.

Table A.1. Titration data of ChOH(CH_3OH) solution.

Mass of ChOH(CH_3OH) Sample (g)	**Volume HCl (mL)**	**n ChOH (mol)***	**Mass of ChOH (g)**	**ChOH Percentage**	**Average %ChOH**
0.3978	13.50	0.0012096	0.1465	36.94	36.87
0.4078	13.70	0.00122752	0.1487	36.46	
0.4041	13.75	0.001232	0.1492	36.92	
0.4030	13.80	0.0012364	0.1498	37.17	

[HCl] = 0.08966 mol.L^{-1}

Table A.2. Kinetic study for temperature 65 °C.

Test	**Time (min)**	**Oil mass (g)**	**ChOH mass (g)**	**Methanol (mL)**	**Organic phase (g)**	**Catalyst phase (g)**
C1	10	20.0138	0.4025	9.18	17.35	2.0843
C2	20	20.0081	0.4019	9.18	12.37	1.0831
C3	30	20.0237	0.3993	9.17	17.24	2.1682
C4	45	20.0432	0.4085	9.19	17.34	0.8570
C5	60	20.0094	0.4035	9.18	15.17	2.3021
C6	120	20.0177	0.4032	9.18	15.98	2.4269

Table A.3. Kinetic study for temperature 55 °C.

Test	**Time (min)**	**Oil mass (g)**	**ChOH mass (g)**	**Methanol (mL)**	**Organic phase (g)**	**Catalyst phase (g)**
C1	10	20.0056	0,3975	9.18	18.319	2.4789
C2	20	20.0121	0,4022	9.18	18.006	1.9639
C3	30	20.0208	0,3985	9.17	18.212	1.4017
C4	45	20.0341	0,4074	9.19	18.486	1.2198
C5	60	20.0073	0,3996	9.18	17.8134	2.5061
C6	120	20.0317	0,4012	9.18	18.2443	2.5661

Table A.4. Kinetic study for temperature 45 °C.

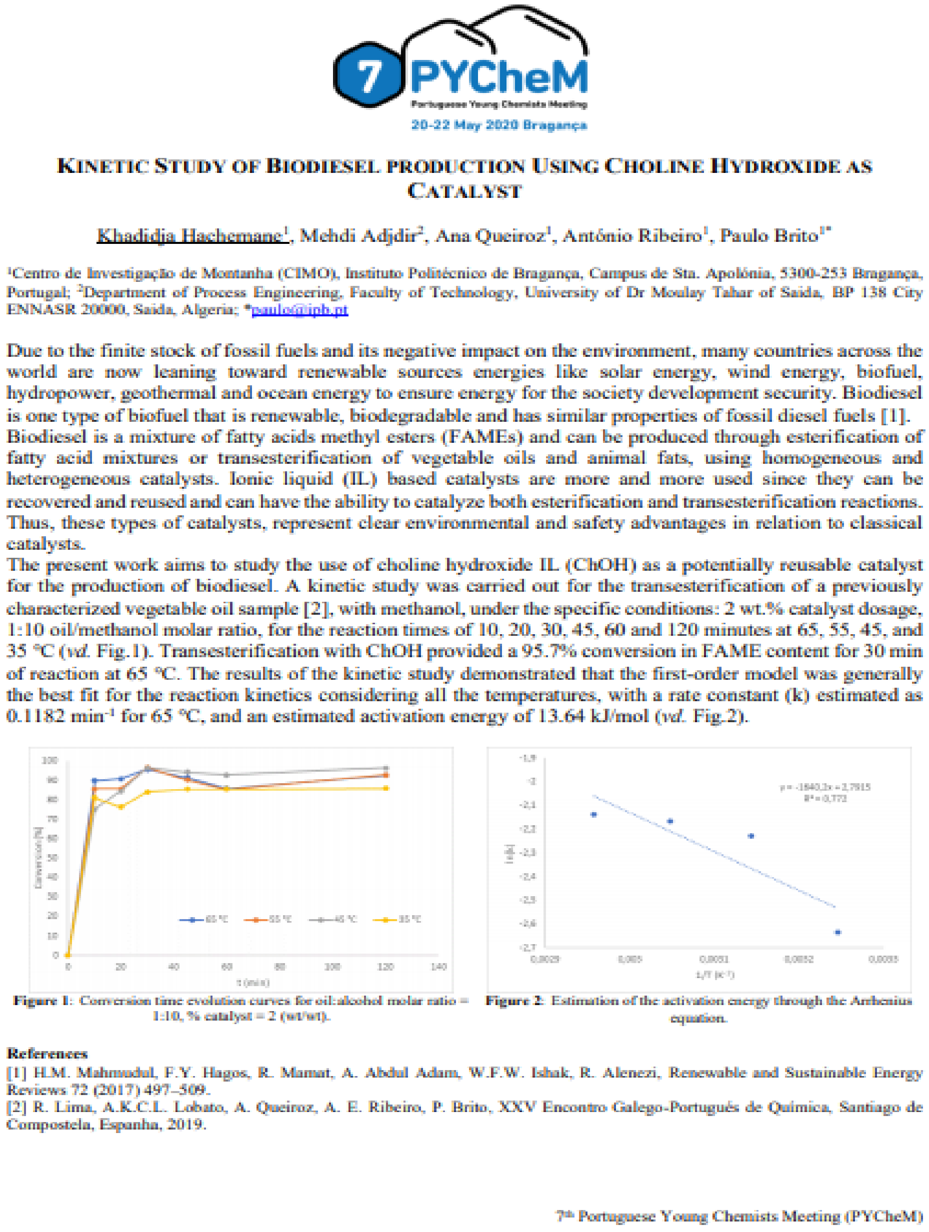
Test	**Time (min)**	**Oil mass (g)**	**ChOH mass (g)**	**Methanol (mL)**	**Organic phase (g)**	**Catalyst phase (g)**
C1	10	20.0064	0,3969	9.18	18.2196	1.6454
C2	20	20.0101	0,4012	9.18	17.9042	0.5240
C3	30	20.0016	0,3993	9.17	18.3684	0.7668
C4	45	20.0276	0,4005	9.19	18.6974	2.1809
C5	60	20.0124	0,4018	9.18	18.4978	2.0937
C6	120	20.0119	0,4002	9.18	18.4334	2.5629

Table A.5. Kinetic study for temperature 35 °C.

Test	**Time (min)**	**Oil mass (g)**	**ChOH mass (g)**	**Methanol (mL)**	**Organic phase (g)**	**Catalyst phase (g)**
C1	10	20.0235	0,4006	9.18	18.2986	1.9289
C2	20	20.0077	0,4016	9.18	18.1765	1.8787
C3	30	20.0170	0,4024	9.17	18.2086	1.9438
C4	45	20.0046	0,4085	9.19	18.1591	2.1946
C5	60	20.0121	0,4028	9.18	17.1299	2.1345
C6	120	20.0024	0,4052	9.18	18.3964	0.4615

APPENDIX B – Conferences

B.1 - 7th Portuguese Young Chemists Meeting 19th – 21st May 2021 Bragança – Portugal.



7 PYCheM
Portuguese Young Chemists Meeting
20-22 May 2020 Bragança

KINETIC STUDY OF BIODIESEL PRODUCTION USING CHOLINE HYDROXIDE AS CATALYST

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Due to the finite stock of fossil fuels and its negative impact on the environment, many countries across the world are now leaning toward renewable sources energies like solar energy, wind energy, biofuel, hydropower, geothermal and ocean energy to ensure energy for the society development security. Biodiesel is one type of biofuel that is renewable, biodegradable and has similar properties of fossil diesel fuels [1]. Biodiesel is a mixture of fatty acids methyl esters (FAMEs) and can be produced through esterification of fatty acid mixtures or transesterification of vegetable oils and animal fats, using homogeneous and heterogeneous catalysts. Ionic liquid (IL) based catalysts are more and more used since they can be recovered and reused and can have the ability to catalyze both esterification and transesterification reactions. Thus, these types of catalysts, represent clear environmental and safety advantages in relation to classical catalysts.

The present work aims to study the use of choline hydroxide IL (ChOH) as a potentially reusable catalyst for the production of biodiesel. A kinetic study was carried out for the transesterification of a previously characterized vegetable oil sample [2], with methanol, under the specific conditions: 2 wt.% catalyst dosage, 1:10 oil/methanol molar ratio, for the reaction times of 10, 20, 30, 45, 60 and 120 minutes at 65, 55, 45, and 35 °C (*vd.* Fig.1). Transesterification with ChOH provided a 95.7% conversion in FAME content for 30 min of reaction at 65 °C. The results of the kinetic study demonstrated that the first-order model was generally the best fit for the reaction kinetics considering all the temperatures, with a rate constant (k) estimated as 0.1182 min^{-1} for 65 °C, and an estimated activation energy of 13.64 kJ/mol (*vd.* Fig.2).

Figure 1: Conversion time evolution curves for oil:alcohol molar ratio = 1:10, % catalyst = 2 (wt/wt).

Figure 2: Estimation of the activation energy through the Arrhenius equation.

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