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EVALUATION OF ALKALINE IONIC LIQUIDS FOR CATALYSIS OF BIODIESEL FROM COOKING OIL

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"A vida é para quem é corajoso o suficiente
para se arriscar e humilde o bastante para aprender."

Clarice Lispector

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ABSTRACT

Biodiesel production is performed in the industry by alkaline transesterification of oils with a low amount of free fatty acids. Aiming to minimize its production costs, low quality, or waste oils have been investigated as an alternative source of triacylglycerols. In order to reduce the disposal of conventional catalysts used industrially, ionic liquids (ILs) have been studied to be applied as catalysts in transesterification, since they can be recovered and reused in next reaction cycles. The main objective of this work was to investigate the application of alkaline type ionic liquids in the catalysis of transesterification reactions of mixtures of triacylglycerols. In the present work, the ionic liquid bis-(3-methyl-1-imidazole)-ethylene dihydroxide (IMC_2OH) synthesis was carried out. The use of the IL choline hydroxide (ChOH) as a catalyst was evaluated in the production of biodiesel through a kinetic modelling study under the specific conditions of 2 wt.% catalyst dosage, 1:10 oil/methanol molar ratio, for the periods of 0, 10, 20, 30, 45, 60, 120, 240, 360, and 480 minutes at 65 °C. A possible way to recover this IL from liquid-liquid extraction with water/butanol and water/ethyl acetate has been evaluated. Due to some challenges occurred in IMC_2OH synthesis, the conversion obtained in the second step of synthesis was lower than expected. Transesterification with choline hydroxide presented 85.21% of conversion in FAME content in 30 minutes of reaction, and the results of the kinetic study which was carried out demonstrated that the second-order model was the best fit for the reaction with a rate constant (k) estimated as 0.2930 $L.mol^{-1}.min^{-1}$. From the recovery of the IL, it was possible to conclude that although there was some separation of it from the glycerol by the extraction with butanol and water, an amount of ChOH remained in glycerol phase. In conclusion, ChOH revealed an excellent capacity for fast transesterification. Thus, based on a more detailed study of the optimal reaction parameters for ChOH and subsequent application of the recovered amount of this ionic liquid in new reaction cycles, there is a strong indication that its reuse as a catalyst is technically feasible for the conversion of triacylglycerols, which enables its possible industrial application.

Keywords: Biodiesel production; Transesterification; Ionic liquids; Imidazolium; Choline Hydroxide.

RESUMO

A produção de biodiesel é realizada industrialmente por transesterificação alcalina de óleos com baixa quantidade de ácidos gordos livres. Com o intuito de minimizar os custos de produção, óleos de baixa qualidade, ou usados, têm sido investigados como alternativa de fonte de triglicerídeos. Para reduzir o descarte de catalisadores convencionais usados industrialmente, líquidos iónicos (LIs) são estudados para serem aplicados como catalisadores na transesterificação, uma vez que podem ser recuperados e reutilizados nos próximos ciclos de reação. O principal objetivo deste trabalho foi o estudo da aplicação de líquidos iónicos alcalinos na catálise de reações de transesterificação de misturas de triacilgliceróis. Neste estudo, o líquido iónico dihidróxido de bis-(3-metil-1-imidazol)-etileno (IMC_2OH) foi sintetizado. O uso do LI hidróxido de colina como catalisador (ChOH) foi avaliado na produção de biodiesel por meio de um estudo de modelagem cinética sob condições específicas de 2% em massa de catalisador, razão molar 1:10 óleo/metanol, para os períodos de 0, 10 , 20, 30, 45, 60, 120, 240, 360 e 480 minutos a 65 °C. Uma possível maneira de recuperar esse LI por meio de extração líquido-líquido com água/butanol e água/acetato de etila foi avaliada. Alguns obstáculos ocorreram na síntese do IMC_2OH, sendo a razão pela qual a conversão obtida na segunda etapa da síntese foi menor que o esperado. A transesterificação com hidróxido de colina apresentou uma conversão de 85.21% em conteúdo FAME em apenas 30 minutos de reação. A partir do estudo cinético realizado o melhor ajuste obtido foi para uma reação de segunda ordem e a taxa de reação (k) foi estimada em 0.2930 $L.mol^{-1}.min^{-1}$. Pela recuperação do LI, foi possível concluir que, embora tenha ocorrido alguma separação do glicerol por extração com butanol e água, uma quantidade de ChOH permaneceu na fase de glicerol. Em conclusão, o ChOH revelou uma alta velocidade de reação nas condições operacionais aplicadas. Assim, com base em um estudo mais detalhado dos parâmetros de reação ótimos para o ChOH e na subsequente aplicação da quantidade recuperada desse líquido iónico em novos ciclos de reação, há uma forte indicação de que sua reutilização como catalisador é tecnicamente viável para a conversão de triglicerídeos, o que possibilitaria sua aplicação industrial.

Palavras-chave: Produção de biodiesel; Transesterificação; Líquidos iónicos; Imidazólio; Hidróxido de colina.

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NOMENCLATURE

Acronyms and symbols

ABIL	Amino-functionalized basic IL
ANP	Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (Brazilian National Agency for Petroleum, Natural Gas and Biofuels)
ANVISA	Brazilian Health Surveillance Agency
AV	Acid Value
B100	Pure biodiesel
B20	Fuel with 20% concentration in biodiesel
DAG	Diacylglycerol
EtOAc	Ethyl Acetate
EU	European Union
FAME	Fatty acid methyl esters
FFA	Free fatty acids
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatography
GC-FID	Gas chromatograph with flame ionization detector
GHG	Greenhouse gas
GL	Glycerol
IL	Ionic liquid
LCA	Life cycle analysis
ME	Methyl ester
MAG	Monoglyceride
NMR	Nuclear magnetic resonance
OA	Oleic Acid
OAPEC	Organization of Arab Petroleum Exporting Countries
PNAER	National Action Plan for Renewable Energy
PNPB	National Program for the Production and Use of Biodiesel
R^2	Coefficient of determination
REN21	Renewable energy policy network for 21st Century
SFO	Sunflower oil
T	Temperature
T_d	Decomposition temperature
TAG	Triacylglycerol
TSIL	Task-specific ionic liquids
UCO	Used cooking oil
WCO	Waste cooking oil
WFO	Waste frying oil
wt	Weight

Formulas

$[BIM]HSO_4$	Butylimidazolium hydrogen sulfate
$[BMIM][MeSO_4]$	1-butyl-3-methyl imidazolium methyl sulfate
$[BMIM]BF_4$	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM]Br	1-butyl-3-methylimidazolium bromide
$[BMIM]HSO_4$	1-butyl-3-methylimidazolium hydrogen sulfate
[BMIM]OH	1-butyl-3-methylimidazolium hydroxide
$[BSMBIM][CF_3SO_3]$	3-methyl-1-(4-sulfo-butyl)-benzimidazolium trifluoromethanesulfonate
$[BSO_3HMIM]BF_4$	1-butylsulfonic-3-methylimidazolium tetrafluoroborate
$[BSO_3HMIM]HSO_4$	1-sulfobutyl-3-methylimidazolium hydrogen sulfate
$[MIM]HSO_4$	Methylimidazolium hydrogen sulfate
BNPs-CCH	CCH stabilized on boehmite nanoparticles
CaO	Calcium oxide
CCH	Chlorocholine hydroxide
CH_3OH	Methanol
ChIm	Choline imidazolium
ChOH	Choline hydroxide
ChOMe	Choline methoxide
CO	Carbon monoxide
CO_2	Carbon dioxide
IMC_2OH	Bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide
KOH	Potassium hydroxide
MeOH	Methanol
NaOH	Sodium hydroxide
NO_x	Nitrogen oxides
SO_x	Sulfur oxides

1. BACKGROUND AND OBJECTIVES

1.1 BACKGROUND

With the discovery and use of new energy sources in the Second Industrial Revolution, the use of petroleum and its derivatives became the primary source of the world energy matrix [1]. In such a way, 5.8 x10^{11} GJ were consumed globally in 2016, of which 81% was derived from coal, petroleum, and natural gas [2].

Although these fossil-based fuels satisfy the energy requirements of the world, the depletion of its energy reserves, the high demand for fossil fuels, and the dependence on it have led researchers to explore sustainable solutions that address these issues to meet our needs. Biofuels have received heightened interest due to positive attributes such as low life cycle greenhouse gas (GHG) emissions, renewable feedstocks, and their non-toxic and biodegradable residues [3–5].

Amongst biofuels, bioethanol, and biodiesel have by far the largest share of the global biofuels market [6]. The advantageous properties of biodiesel, such as low Sulphur content, lack of aromatics, higher lubricity, higher flash point and compatibility with the existing petroleum diesel distribution infrastructure make it a viable alternative for the fuel to be a blended component in the transport sector [3,7,8].

However, despite its satisfactory properties, economic reasons have been one of the significant obstacles to its commercialization. In this scenario, there are several concerns related to first-generation biodiesel (derived from food crops), including limited arable land, the fuel vs. food/feed competition over crops, which lead to increased costs of food. In this regard, second-generation biodiesel production has a considerable potential to provide benefits such as reduction of waste residues and the reduction of greenhouse gas (GHG) emissions by replacing fossil fuels [8,9].

The second-generation biodiesel is derived from non-edible resources or biomass, including either waste cooking oil (WCO), grease, and animal fat, or non-edible energy crops [8]. The application of WCO as feedstock for biodiesel production is perceived as one of the potential ways of effectively reducing the cost of producing biodiesel. Currently, the fuel costs about 1,5–3 times higher than diesel, of which the price of oil feedstocks, could contribute up to 70–95% of the production costs [10,11].

Hereof, the production of biodiesel from waste oils and the application of ionic liquids as a catalyst are modern alternatives to overcome the disadvantages of the traditional production process.

1.2 OBJECTIVES

1.2.1 Main Objectives

Study the application of alkaline type ionic liquids in the catalysis of transesterification reactions of mixtures of triacylglycerols.

1.2.2 Specific Objectives

i. Study biodiesel production catalysed by alkaline ILs such as bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide and choline hydroxide;

ii. Perform kinetic studies of the transesterification reaction to biodiesel production using alkaline ILs;

iii. Study the possibility of recovering the ILs after each reaction cycle.

1.2.3 Document Structure

This master thesis report is organized into six 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 emphasizes the current situation of biodiesel in Portugal and Brazil. In addition, it contains a state of the art about the advantages and disadvantages of using biodiesel, its physicochemical properties, current and advanced production methods of this fuel, as well as the catalysts used in its production.

Chapter 3 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.

Concerning the experimental section, Chapter 4 describes the equipment, reagents, and experimental procedures, highlighting the process for the synthesis of the ionic liquid IMC_2OH and the study of choline hydroxide recovery.

With respect to the experimental results obtained and the appropriate discussion on the synthesis of bis-(3-methyl-1-imidazole)-ethylene dihydroxide, the characterization of the raw material, the kinetic study with ChOH and the investigation on the attempt to recover this ionic liquid are presented in Chapter 5.

Finally, Chapter 6 summarizes the main conclusions as well as the suggestions for future research.

2. BIODIESEL

Biodiesel consists of Fatty Acid Methyl Esters – known as FAME – produced by a wide variety of renewable lipid feedstocks, such as vegetable oils and animal fats. The term “Bio” refers to its renewable and biological source in contrast to traditional fossil fuel. Further, the word “Diesel” expresses its use in powering diesel engines [12,13]. The most widely used industrial method for the production of biodiesel is transesterification, which refers to a catalysed chemical reaction involving vegetable oil and alcohol [13–15].

2.1 ADVANTAGES AND DISADVANTAGES OF BIODIESEL

Among the attractive features of biodiesel, the most taken into account are that it can be used in conventional compression-ignition engines as it demonstrates similar characteristics to petroleum diesel, and it can be blended with diesel creating a stable fuel blend [4,7].

Moreover, although the oxygen content in biodiesel is responsible for the increase in CO_2 and NOx emissions [16–18], it is well established that the use of biodiesel affords a substantial reduction in SOx, CO emissions and particulate matter (PM) emissions on combustion compared with diesel [4,9,19–21]. The higher cetane number and the intrinsic oxygen of biodiesel enhance the combustion process which leads to reductions in HC, CO, and smoke formation by 20%, 30%, and 50% respectively on average [16].

General trends observed with biodiesel fuel are the increase in emissions of NOx and CO_2 approximately by 12% and 14% respectively [16]. Although there is an increase in CO_2 emissions from biodiesel when compared to diesel, its life cycle of CO_2 emissions is considered lower. Because when it is produced from plants, the carbon amount released during the fuel combustion is equivalent to the amount of carbon sequestered during the growth of the biomass from which it was derived [9,22].

On the other hand, the current major challenge in making biodiesel production economically viable is the high price of the vegetable oils compared to diesel [11,23]. Appropriate selection of feedstock is one of the crucial factors for reducing the cost of biodiesel since 70-95% of the biodiesel price is due to the cost of raw material. Therefore, the application of waste cooking oils (WCO) as feedstock to reduce the cost of producing biodiesel is a strategy to circumvent this issue [11,24].

2.2 BIODIESEL CURRENT SITUATION

2.2.1 Situation in Brazil

Brazilian federal government launched in December 2004 the *Programa Nacional de Produção e Uso do Biodiesel (PNPB)* - National Program for the Production and Use of Biodiesel - with the initial objective of introducing biodiesel into the Brazilian energy matrix. In 2008, the legally binding mixture of 2% entered into force throughout the national territory, and the proportion of biodiesel added to diesel oil increased to 12% in March 2020 [24].

In 2017, the national production was 4.3 billion liters which were 56.2% of the total capacity. Figure 1 represents the evolution of biodiesel production from 2008 to 2017 [25].

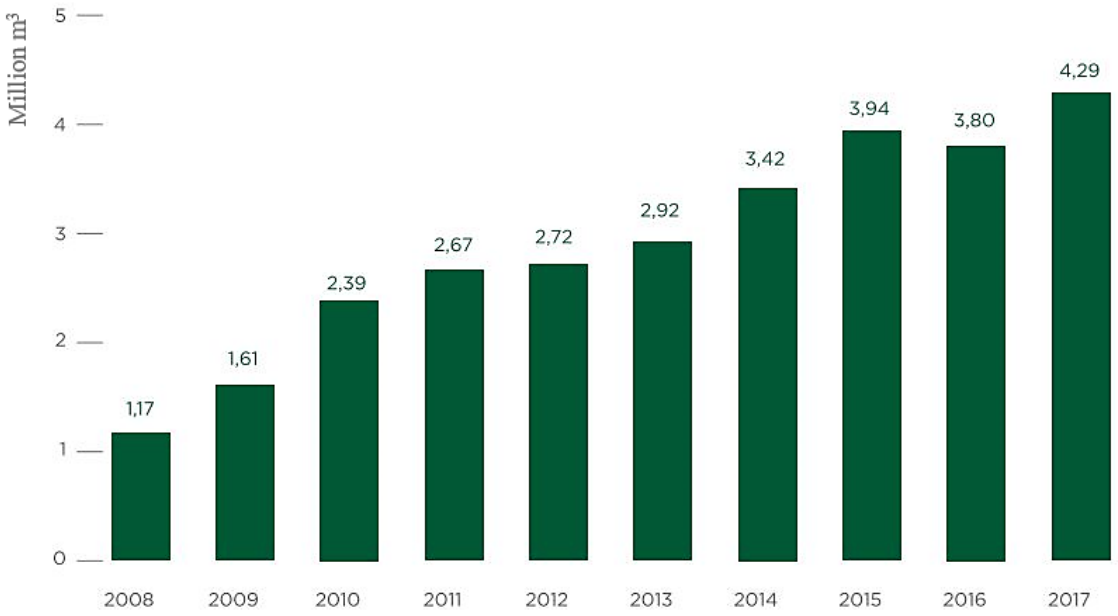

Figure 1. Biodiesel production evolution in 2008-2017.
Source: ANP, (2018) [25].

Concerning the raw material of the produced biodiesel, in 2017, soybean continued to be the primary material for biodiesel production (B100), with an equivalent to 71.6% of the total, an increase of 1.7% compared to 2016. The second raw material in the production ranking was animal fat (16.8% of the total), followed by other fatty materials (11.3% of the total) and cotton oil with 0.3% of participation [25]. In Figure 2

is illustrated the raw materials used in biodiesel production from 2008 to 2017, as can be seen, soybean oil is the most used material among all.

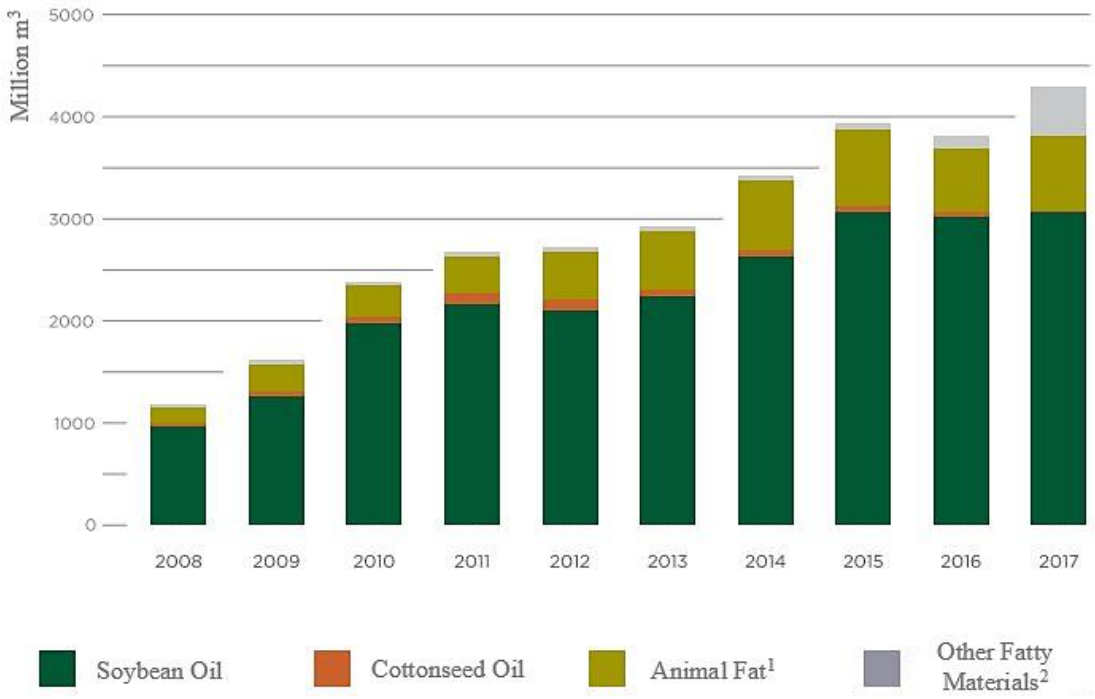

Figure 2. Raw materials used in biodiesel production in 2008-2017.
1 Includes beef fat, chicken fat and pork fat.
2 Includes palm oil, peanut oil, forage turnip oil, sunflower oil, castor oil, sesame oil, used frying oil and other fatty materials.
Source: ANP, (2018) [25].

To conclude, in Figure 3 is represented the nominal capacity and the biodiesel (B100) production, in thousand m^3 per year, by Brazilian regions in the year 2017. As can be seen, the Midwest is the most significant producer region, representing 44.2% of total production, due to the vast availability of raw materials.

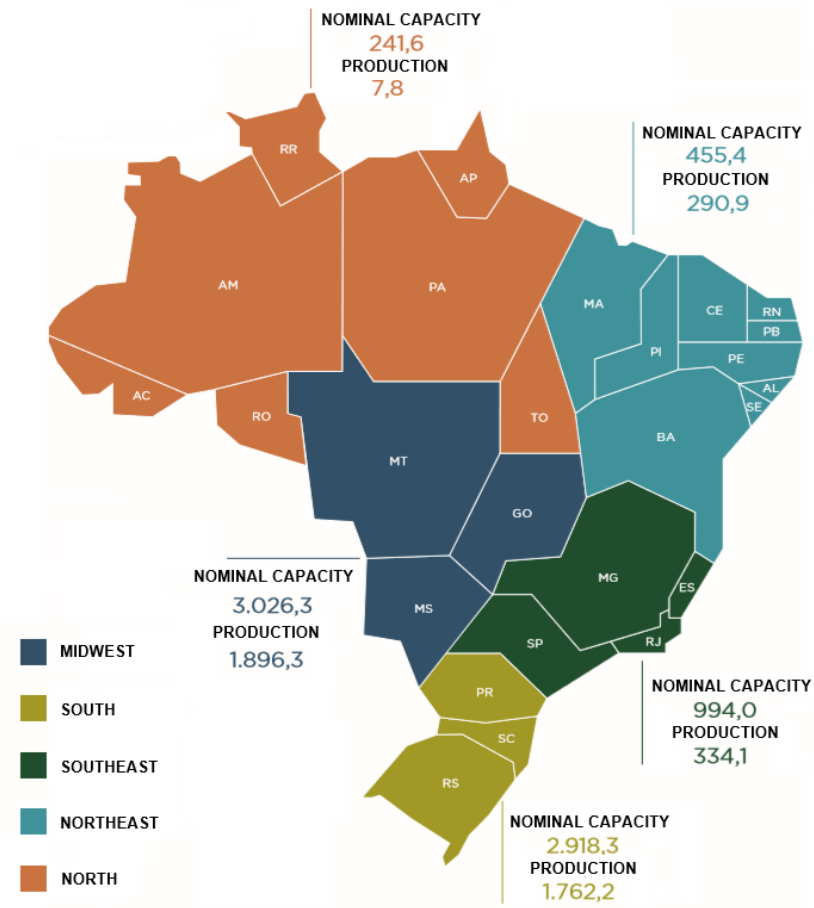

Figure 3. Nominal capacity and biodiesel (B100) production by Brazilian regions in 2017. Source: ANP, (2018) [25].

2.2.2 Situation in Portugal

According to the global status report of REN21 [26], 11.8 billion liters of biodiesel were produced by the European Union (EU) in 2017, corresponding to 38.44% of the global production (30.7 billion liters).

The European Union has defined through the Directive 2009/28/CE [27] on the promotion of the use of energy from renewable sources, the goal of achieving a 20% share of energy from renewable sources in consumption by 2020, and a percentage of 10% in the transport sector.

In Portugal, the legislation which partially transposes the Directive 2009/28/CE is the National Action Plan for Renewable Energy for the period 2013-2020 (PNAER 2020), which sets the target of 31% for the use of renewable energy in final gross energy consumption and 10% for energy consumption in transport by 2020 [28].

The PNAER 2020 indicates a set of temporary goals for the use of renewable energy in gross final consumption: 22.6% for the years 2011 and 2012; 23.7% for 2013

and 2014; 25.2% in 2015 and 2016; and 27.3% for the years 2017 and 2018. In this regard, as shown in Figure 4, in 2017 the incorporation of renewable energy sources in gross final consumption stood at 28.1%, showing that Portugal has already reached 90.6% of its target for 2020 in 2017. Comparing the results obtained by Portugal with the rest of EU-28 countries, it was verified that Portugal registered the 7th best position in 2017 [28].

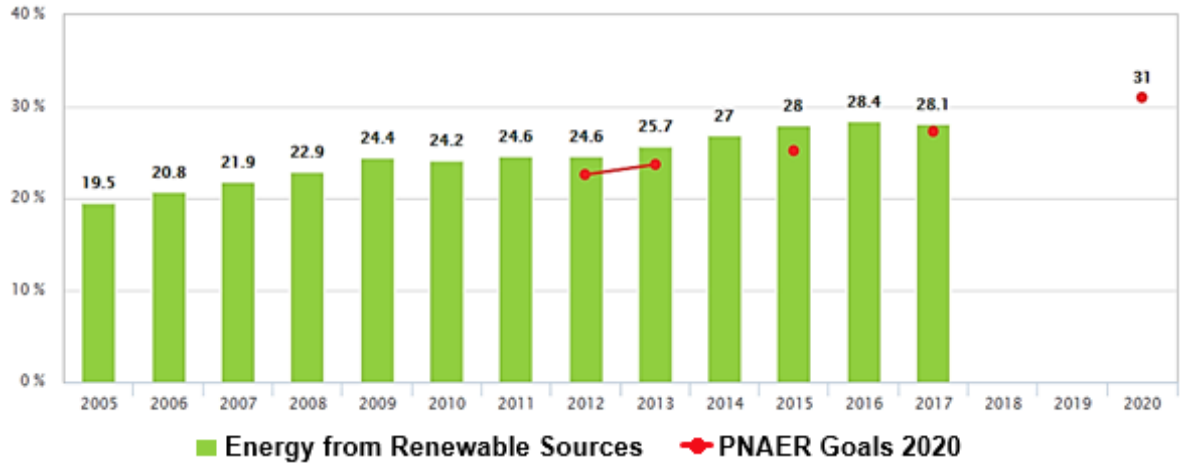

Figure 4. Evolution of the minimum trajectory of renewable sources energy in the gross final consumption of energy.
Source: REA, (2019) [28].

Since the transport sector is one of the most dependent on fossil fuels, Portugal increased the share of fuels from renewable energy in this sector. Figure 5 demonstrates this increase in the last years, and in 2017, 7.93% of renewable energy sources in transport were achieved, surpassing the EU-28 average (7.56%) [28].

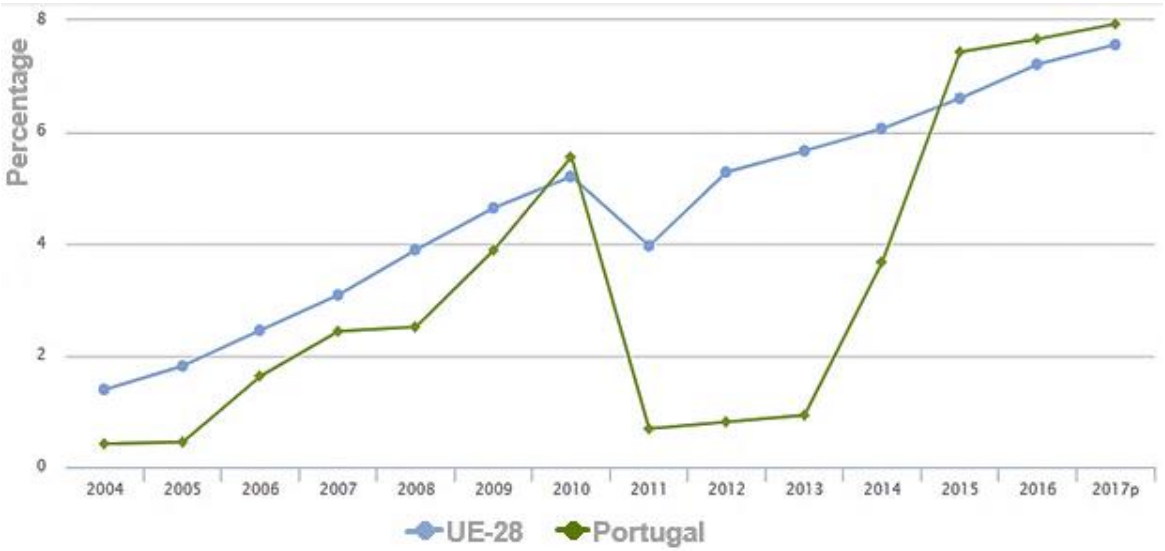

Figure 5. Percentage of renewable energy in transport fuel consumption in Portugal and EU-28.
Source: REA, (2019) [28].

Also, with respect to liquid biofuels, its production in the EU has increased significantly, being biodiesel the liquid biofuel most widely produced, followed by bio-gasoline and other liquid biofuels [29]. According to the Portuguese Entity, *Entidade Nacional do Setor Energético (ENSE)* [30], in 2019, the national production of FAME was 402 million m^3. The monthly output distribution can be seen in Figure 6, verifying that the average monthly value was approximately 33,000 m^3.

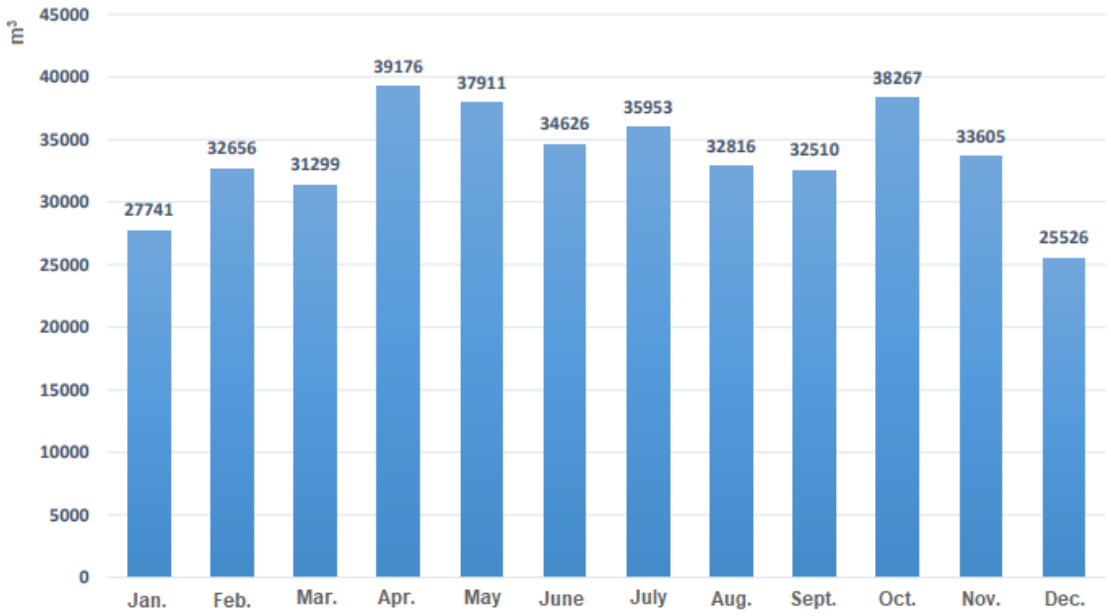

Figure 6. FAME production in Portugal in 2019.
Source: ENSE, (2020) [30].

Rapeseed oil was still the dominant biodiesel feedstock in the EU, accounting for 45% of total production in 2017. However, its share in the feedstock mix has considerably decreased compared to the 72% share in 2008, mostly due to the higher use of recycled vegetable oil/waste cooking oil (WCO) which came in the second-most important feedstock in 2017. In this year, the largest EU producers of used cooking oil, UCO-methyl ester, were the Netherlands, Germany, and the United Kingdom. Palm oil came in third place in terms of feedstock used in 2017 (18%) [31].

In December 2018, the revised renewable energy directive 2018/2001/EU [32] entered into force, as part of the Clean energy for all Europeans package, setting the framework of the renewable energy policy for the period 2021–2030 and thus, helping the EU to meet its emissions reduction commitments under the Paris Agreement. The recast directive establishes a new binding renewable energy target for the EU for 2030 of at least 32%, with a clause for a possible upwards revision by 2023.

Regarding the incorporation of biofuels into fossil fuels, Decree-Law No. 117/2010, of 25 October [33] defines the limits of mandatory integration of biofuels from 2011 to 2020. Under the terms of article 307 of Law No. 71/2018, of December 31 [34], the clause e) of the Decree-Law which required 10% of incorporation in 2019 and 2020 was derogated, and the incorporation target was fixed at 7.0% in energy content.

2.3 BIODIESEL PHYSICOCHEMICAL PROPERTIES

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 [3,19,35]. 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 [19,23].

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 [3].

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 [23,36].

These biodiesel properties mentioned above must be comparable to diesel oil to ensure that it can be used in diesel engines without any modification. The physicochemical properties of biodiesel produced from different sources, as well as diesel oil ones, are summarized in Table 1.

Table 1. Physicochemical properties of biodiesels from several feedstocks compared to petroleum diesel.

Oil source	**Biodiesel from edible oils**		**Biodiesel from inedible oils**		**Biodiesel from waste oils**		**Petroleum diesel**	
Property	Soybean oil	Palm oil	Cottonseed oil	Jatropha oil	Palm oil	Rapeseed oil	Petroleum diesel	EN 14214 limit
Density at 15 °C $\left(\frac{kg}{m^3}\right)$	913.8	864.42	876.7	879.5	877.2	895	839	860-900
Heating value $\left(\frac{MJ}{kg}\right)$	39.76	-	40.43	39.23	39.87	36.70	45.825	Min. 35
Cloud point (°C)	9	16	7	2.7	-	-	2	-
Flash point (°C)	76	135	153	135	130	192	71.50	>101
Pour point (°C)	2	15	6	2	10	-	1	-
Viscosity at 40 °C $\left(\frac{mm^2}{s}\right)$	4.039	4.50	4.11	4.80	6.32	9.48[a]	2.91	3.5-5.0
Cetane number	37.90	54.60	36.5	51.6	62	53	49.70	Min. 51
Acid value $\left(\frac{mg}{g}\right)$	0.266	0.24	0.19	0.40	-	-	0.17	Max. 0.5
Sulfur content % $\left(\frac{m}{m}\right)$	0.8	0.003	1.9	1.2	-	0.002	0.05	-

[a]30°C

Source: Abdalla, (2018) [19]; Dharma et al., (2016) [3], Fukuda, Kond and Noda, (2001) [20].

2.4 BIODIESEL PRODUCTION

2.4.1 Raw Materials Used in Biodiesel Production

For biodiesel production, several raw materials can be employed, such as vegetable oils, animal fats, algae oils, and microbial oil sources. Feedstocks can be

screened based on their availability and type of source (edible, non-edible, or waste), plus, the selection of these materials is a crucial step in biodiesel production, which affects some factors, including cost, yield, composition, and purity of the produced fuel [4,7]. Table 2 illustrates the advantages and disadvantages of each feedstock type aforementioned.

Table 2. Advantages and disadvantages of different raw materials used in biodiesel production.

Feedstock	Advantages	Disadvantages
Edible Oils	Do not require pre-treatment	Expensive final product
	High heat content	Competition with the food market
Inedible Oils	No competition with the food sector	Low yields due to free fatty acids content
	Reduced biodiesel production cost	
	Less requirement of land for cultivation	Need to purify the final product
Waste Oils	Cheaper than commercial vegetable oils	High content of free fatty acids
	No competition with the food sector	High water content
Animal Fat	Availability in large quantity	Presence of free fatty acids
	Low cost	Product non-viability at low temperatures due to its high viscosity
Algae	A high percentage of oil content	Necessary upstream and downstream processes (dehydration of algae, oil extraction, and product purification)
	Less effect on food chain balance	

Source: Ambat et al., (2018) [7]; Fonseca et al., (2019) [37]; Nurfitri et al., (2013) [38]; Sun et al., (2017) [39].

Since the chemical composition of fatty acids in oils is based on the source from which it is derived, Table 3 briefly describes the fatty acid distribution for different generations' oil feedstocks. Palmitic (16:0) and stearic (18:0) are the two most common saturated fatty acids. Similarly, oleic (18:1), linoleic (18:2) and linolenic (18:3) are the most common unsaturated fatty acids [7,40].

Regarding the biodiesel production using waste cooking oil, there are two types: yellow and brown grease. The components in cooking oil can contain animal fat, fish fat

or vegetable oil, depending on the food which was fried or cooked in it. Yellow grease contains less than 15% fatty acid and can be a potential low-cost material for biodiesel production. In contrast, brown grease has a higher content of water and free fatty acids (> 15%), which has an adverse effect on biodiesel production [7].

Table 3**.** Fatty acid distribution among different feedstock.

Feedstock	Type	Fatty Acid Distribution (wt.%)					
		Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Rapeseed	Edible Oil	-	1-3	0-1	10-15	12-15	8-12
Soybean	Edible Oil	-	6-10	2-5	20-30	50-60	5-11
Palm	Edible Oil	0.5-2	39-48	3-6	35-44	9-12	-
Jatropha	Inedible Oil	14.1-15.3	0-13	-	34.3-45.8	14.1-15.3	0-0.3
Cottonseed	Inedible Oil	-	22.96-28.33	0.8-0.9	13.27-18.3	-	0.2
Yellow Grease	WCO	2.43	23.24	12.96	44.32	6.97	0.67
Brown Grease	WCO	1.66	22.83	12.54	42.36	12.09	0.82
Chicken Fat	Animal Fat	3.1	19.82	3.06	37.62	-	-
Tallow	Animal Fat	23.3	19.3	42.4	2.9	0.9	2.9

Source: Adapted from Ambat et al. (2018) [7].

2.4.1.1 Waste oils

Acylglycerol (i.e. esters formed from glycerol and fatty acids) constitution of used cooking oil or animal fat is similar to that of vegetable oils. However, differences in fatty acid profiles of oil due to the frying process have a significant influence on the quality of the biodiesel produced from these oils as compared to that from refined vegetable ones [41].

Waste oil can be obtained from cooking oil, animal fat, and sludge oil. Frying oil is repeatedly exposed to high temperatures (150 to 200 °C) in the presence of oxygen, moisture, pro-oxidants and antioxidants of food. The heating process leads to the formation of many compounds, which vary according to the composition of the oil and food and, especially, increase the free fatty acids content. This process also changes the oil color to dark brown or red, increase the viscosity and specific heat, change surface

tension and increase the tendency of fat to form foam. During the frying process, the oil can undergo several chemical reactions such as polymerization, hydrolysis, and oxidation owing to their reaction to light, heat, and oxygen [11,37].

Besides the degraded products, oxidation produces hydroperoxides, aldehydes, and ketones. The polymerization is a chemical reaction in which unsaturated fatty acids react to form dimers (a molecule composed of two identical subunits of monomers linked together) and polymers of triacylglycerols. Consequently, the oil molecular weight rises, and the oil becomes more viscous. Furthermore, in hydrolysis, FFAs are created because triacylglycerols are broken down, as well as monoacylglycerols and diacylglycerols [39,41,42].

Since the effectiveness of alkaline transesterification process depends on the quality of the vegetable oil used for transesterification, it is recommended a pre-treatment when the FFA level of the feedstock exceeds 1 wt.% and 0.5 wt.% for water to avoid the problem of possible saponification reaction which hinders separation of the ester from glycerin reducing the yield. The pretreatment methods include steam distillation, extraction by alcohol, and mainly acid-catalytic esterification [41,42].

2.4.1.1.1 First and second-generation oils

Biofuels are divided into categories, and biodiesel is classified in generations with respect to the raw material from which it was produced [23,43]. Waste oils are considered an economic and increasingly available second-generation alternative in biodiesel synthesis. Currently, refined vegetable oils are the primary industrial feedstock for biodiesel production, but the relatively high and unstable prices of these food-grade raw materials constitute an obstacle for biodiesel production and commercialization [8,40,44].

Waste frying oils can be a low-cost and sustainable feedstock, maximizing the use of the existing infrastructure, and reduce dependence on food crops as fuel feedstocks because they are generated in large quantities during food or semi-product preparation by frying in industrial environments. Additionally, the EU has banned the use of waste cooking oil as animal feed due to the concern on animal health and the subsequent food chain. Therefore, WCO disposal has become an issue in most countries. This residue cannot be discharged into drains or sewers because it leads to blockages and may also pollute watercourses leading to problems for wildlife. Besides that, it is also prohibited

and cause problems if it is dumped in municipal solid waste landfill and municipal sewage treatment plant [8,45,46].

2.4.2 Biodiesel Production Methods

The direct use of crude oil and fat produced from vegetable and animal sources is considered impracticable for diesel engines due to their high viscosity, as well as polyunsaturation character, low volatility, poor fuel atomization, incomplete combustion, insufficient mixture formation inside the combustion chamber and formation of carbon deposits [15,20]. Alternatively, biodiesel can be employed in compression ignition engines, either in its pure form or blended forms by its advantageous properties such as low sulfur content, lack of aromatics, higher lubricity, and very high cetane values [11,14,35,47].

Therefore, a strategy to overcome the obstacle associated with the direct use of oils is to use, mainly, techniques known as esterification, and transesterification. In fact, nowadays, in most industrial units, biodiesel is produced through transesterification of edible oil and methanol using homogeneous basic catalysts in stirred-tank reactors [48,49]. Other possibilities but not widely used today are microemulsification and pyrolysis [7,15,44].

2.4.2.1 Esterification

Oils are also composed, to a lesser extent, by carboxylic acids – known as free fatty acid in biodiesel production – which can be converted to fatty acid esters in the presence of a catalyst by esterification, as shown in Figure 7. The esterification reaction of oils can then be used both as direct biodiesel production and as pre-esterification of FFAs, which is commonly used to decrease its levels in high-FFA feedstocks before they can be used in base-catalysed transesterification. In addition, the esterification of fatty acids with low molecular weight alcohols is commercially achieved using liquid catalysts, such as sulfuric acid and hydrofluoric acid [15,48,49].

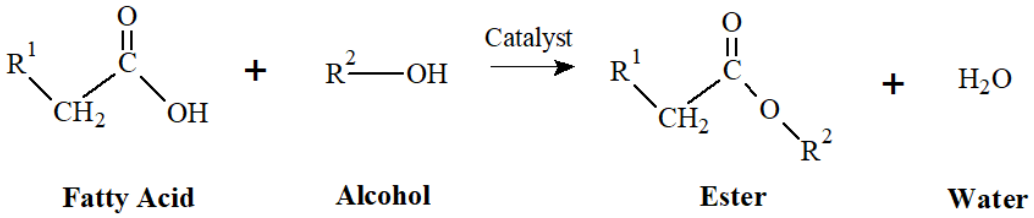

Figure 7. Scheme of the esterification reaction.
Source: Adapted from Andreani and Rocha (2012) [15].

2.4.2.2 Transesterification

The biodiesel transesterification consists of a reaction between triacylglycerols with an alcohol producing the fuel itself and glycerol as a by-product. Methanol is frequently employed due to its low cost in most countries and some of its properties such as polarity and small molecular size. Also, particularly in Brazil, ethanol has a more significant potential for utilization in triacylglycerol transesterification due to its availability. More specifically, the transesterification process is a sequence of three consecutive reversible reactions. The first one converts the triacylglycerol into a diacylglycerol. Then, in the second one, monoglyceride is produced from the diacylglycerol. Finally, glycerol is obtained from the monoglyceride [4,15]. For a reasonable conversion rate, this reaction requires the use of a catalyst that can be an acid, an alkaline metal hydroxides, alkoxides, and non- ionic bases [7,50]. Currently, most of the biodiesel production uses alkaline catalysts and, industrially, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are preferred due to their wide availability and low cost, and sodium methoxide is also used to obtain faster reactions [37,44].

Figure 8 describes the transesterification reaction between triacylglycerol and alcohol. The letters R^1, R^2, R^3, denote alkyl groups present in the triacylglycerol and R^4 represents an alkyl group in the alcohol.

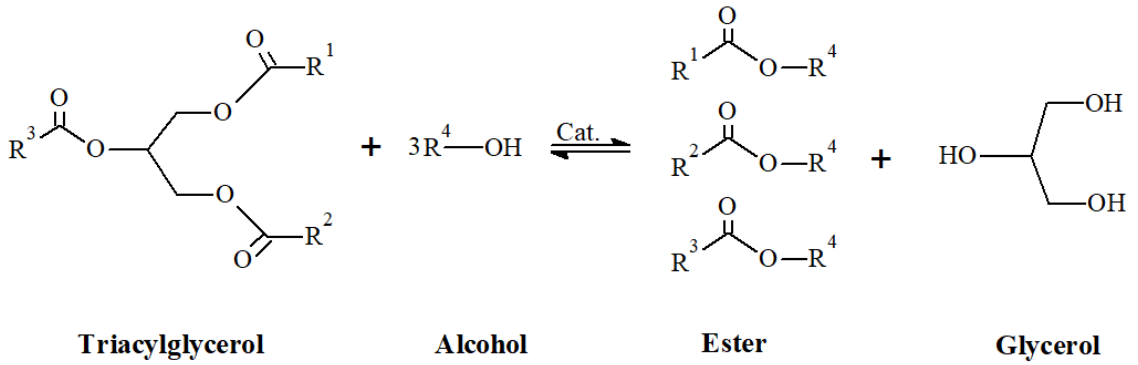

Figure 8. Scheme of the transesterification reaction.
Source: Adapted from Fonseca et al. (2019) [37]; Mumtaz et al. (2016) [4].

As shown in Figure 8, the stoichiometry dictates that it is necessary three moles of alcohol for each mol of triacylglycerol to achieve a stoichiometric conversion. However, it is common to use much higher alcohol molar ratios due to the reversible nature of the reaction [15,51].

The transesterification chemical pathway for a basic-catalysed reaction is shown in Figure 9. First, an alkoxide ion is created (1), the production of this active species is what gives rise to a different chemical pathway for the reaction compared to a reaction catalysed by acid. The alkoxide acts as a strong nucleophile which attacks the carbonyl group in the triacylglycerol, forming a tetrahedral intermediate (2). Then the tetrahedral structure undergoes structural reorganization to form alkyl ester and an anion which corresponds to the diacylglycerol (3). Also, the active species is regenerated so that a new catalytic cycle can be started (4), and the sequence is repeated twice [4,7,52].

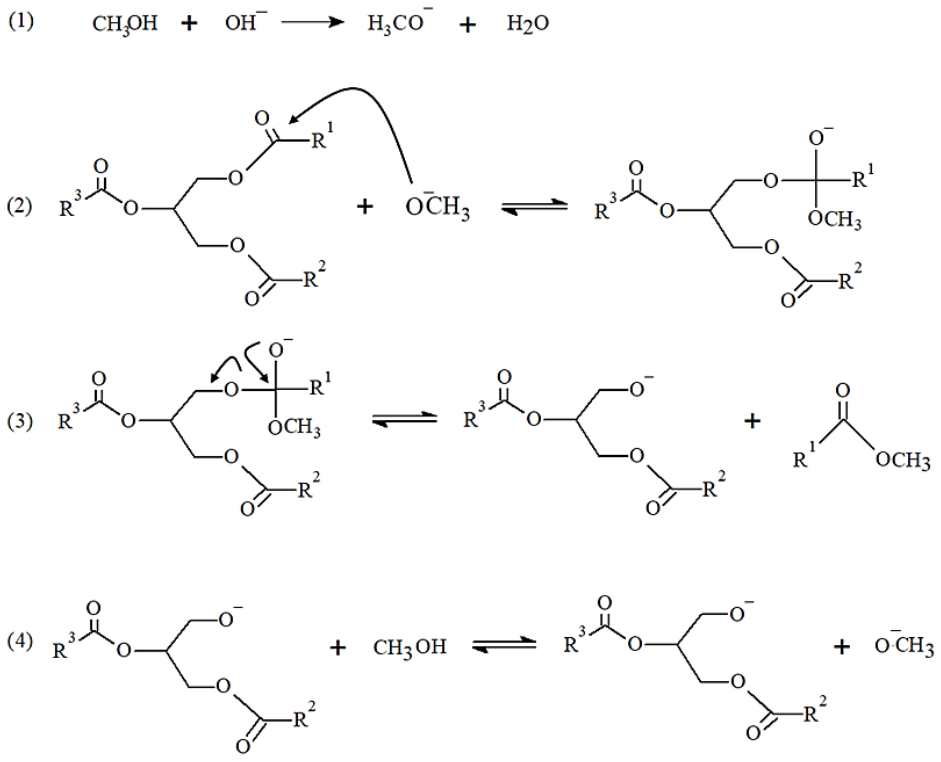

Figure 9. Base-catalysed reaction mechanism for transesterification of triacylglycerols.
Source: Adapted from Lotero (2005) [52].

2.4.3 Catalysts Used in Biodiesel Production

The nature of the catalyst chosen for the conversion of oils to biodiesel is fundamental since it determines the reaction conditions and post-separation steps. The industrially homogenous based catalysed process is preferred due to its fast conversion, and NaOH is utilized because of its high activity, affordability, and low molecular weight [37,52].

For instance, the homogenous based catalysed process is mainly used due to a low reaction time required, the possibility of the reaction be performed at low temperature and pressure and the fact that it is more efficient compared to heterogeneous catalysts. However, to successfully use the base catalysts, it is recommended that oils and other reagents used do not contain water, and high levels of free fatty acids, due to the occurrence of the saponification reaction of triacylglycerols, which inhibit separation of esters and glycerin [7,15].

Reactions with homogenous acid catalysts are insensitive by the amount of FFA in oils. In fact, these catalysts are capable of esterifying the FFA and transesterifying the triacylglycerols simultaneously. Nonetheless, acid-catalysed reactions have a comparatively slower reaction rate. Thus, the acid catalysis requires the use of large quantities of alcohol in order to obtain biodiesel in satisfactory yields [7,15,37].

Compared to homogeneous catalysts, heterogeneous catalysts separation is easy, and it is reusable [7]. Basic heterogeneous catalysts are generally composed of metal oxides, alkaline zeolites, and clays, and they are applied in reactions in which high purity and low content of FFA and water feedstocks are used. These catalysts generally show more active sites than heterogeneous acid catalysts. Its main drawback is associated with the leaching of the active sites after the reaction that reduces their catalytic activity [37].

Heterogeneous acid catalysis is performed by inorganic, polymeric materials, and sulfonated carbons. They are less sensitive to the presence of FFA, and they can be applied as a pre-treatment to reduce the FFA content, or at higher temperatures, simultaneously esterify FFA and transesterify the triacylglycerols without soap formation. Although, due to their lower activity, elevated reaction temperatures are required, increasing the energy consumption of the process [37].

There is also the enzymatic transesterification using lipase as a catalyst. This catalysis can tolerate free fatty acid and water without soap formation, making the separation of biodiesel and glycerol easier. Despite the possible reuse of the catalyst, this enzymatic technology shows a high cost as a result of the enzymes' value along with restricted operation temperature due to the denaturation of enzymes at high temperatures [7,44].

Among the alternatives to overcome the disadvantages of previous catalytic systems, the use of ionic liquids as catalyst appears to be quite promising and environmentally responsible, because the possible recycling of these catalysts at the end of the reaction can be the key to waste minimization [15,53]. Compared to conventional liquid and solid catalysts, ionic liquids exhibit many advantages, such as high thermal stability, low volatility, and high catalytic activity [53,54]. Their main disadvantages are related to the high temperatures used with some ionic liquids and the possibility of deactivation due to glycerol formed [37].

2.4.4 Advanced Biodiesel Production Methods

Due to the use of homogeneous alkaline catalysts such as sodium and potassium methoxides and hydroxides in traditional technology for biodiesel production, it is necessary washing steps to separate the spent catalyst from FAME and the glycerol phase, which makes the manufacturing process of biodiesel unsustainable.

Hence, advanced processes have also been designed. Within the scope of transesterification, there is the supercritical methanol technology (non-catalytic transesterification/esterification) and the microwave technology for the transesterification reaction.

The first one involves the manipulation of the solvents' physical properties which can be achieved by modifying exclusive parameters of the fluid as temperature or pressure. Thereby creating a condition in which the miscibility of methanol and oil is elevated, and they behave as a single phase. This technique displays fast reaction rates, high yield and simpler purification compared to the conventional process. Its main disadvantage is the technology requires very high temperatures (350–400°C) and pressures (200–400 bar) [7,44].

The second one consists in mixing reactants (alcohol, an oil, and a catalyst) using a stirrer device and microwave heat source is applied for the necessary reaction time. Microwave technology demonstrated to be energy efficient compared to conventional heating in continuous biodiesel production showing high FAME yields in a short time. However, the main drawback of this technology is scaling-up to the industrial production scale as well as process safety [7,44].

In addition, the transesterification process can be used with ultrasound-assisted and membrane technology. Ultrasound-assisted technique mixes phases of oil and alcohol efficiently through cavitation, which is favourable for the reaction. It also raises the mass transfer rate, which results in a high yield. However, this process leads to soap formation, and a large amount of wastewater is produced when excess catalyst, soap, and glycerin are washed after the reaction [7,44].

Membrane technology combines membrane separation with a transesterification reaction to make the membranes capable of removing the products formed during the process. Easy removal of products, resulting in high-quality biodiesel is the main advantage of the membrane reactor. Although the use of membrane technology has shown to be promising, soap formation (when a homogeneous alkaline catalyst is used), slow

acid-catalysed reaction rate and membrane systems limitation by pore size and shape of materials still have to be solved [7,44].

Table 4 summarizes the main advantages and disadvantages of many biodiesel production technologies, and Table 5 summarizes the pros and cons of different ways of catalyzing the transesterification reaction.

Table 4. Summary of benefits and limitations of several biodiesel production technologies.

Production Technologies	Benefits	Limitations
Pyrolysis	Simple process	Requires high temperature
		Expensive apparatus
	Pollution-free process	Low purity due to the intolerable amount of carbon residues
Microemulsification	Simple process	High viscosity
		Poor volatility and stability
Microwave Technology	Short time reaction	Problems with scaling-up to the industrial production scale
	Limited heat loss	
Super Fluid Method	Less reaction time	High energy consumption
	High conversion	
	No catalyst required	High apparatus cost
Enzymatic Transesterification	Easy biodiesel recovery	Restricted operation temperature
	Catalyst can be reused	The high cost of enzymes
Traditional Transesterification	Suitable for industrial production	Efficient conversion
		Low cost
	Fuel properties are comparable to diesel	Applicability for feedstock with water

Source: Adapted from Ambat et al., (2018) [7]; Luque and Melero, (2012) [55]; Mumtaz et al., (2016) [4].

Table 5. Advantages and disadvantages of the catalyzing methods of transesterification reaction.

Method	Advantages	Disadvantages
Homogeneous Base-catalysed	High yield	Formation of soap
	Low cost	Generation of wastewater
	Fast reaction rate	
Homogeneous Acid-catalysed	Conversion of FFA to biodiesel	A large amount of alcohol required
	Low cost	Slower reaction rate
Heterogeneous Base-catalysed	Easy separation	Catalyst leaching and low surface area
	Reusability of catalyst	Used with feedstocks of low content of FFA and water
Heterogeneous Acid-catalysed	High temperature	Low concentration of active sites
	Less sensitive to FFA	High energy consumption
	Fast reaction rate	
Ionic Liquid	Reusability of the catalyst	High temperature
	Possibility of several functional groups	Possible deactivation due to glycerol
	High catalytic activity	

Source: Adapted from Fonseca (2019) [37].

3. IONIC LIQUIDS

Ionic liquids (ILs) are described as organic salts that are usually liquid at room temperature due to its melting temperature of below 100 °C [15,53,56]. These liquids are produced through different combinations of cations and anions, and the physicochemical and thermal properties of ILs are influenced by the types of ions used. The cations in ILs are organic with larger molecular volumes, while anions can be organic or inorganic [57,58]. The manipulation of ILs functional groups is their most interesting characteristic because it can be applied to produce task-specific ionic liquids (TSILs) for different applications since the cations control physical properties of ionic liquids (such as density, viscosity, and temperature of fusion). In contrast, the anions govern the chemistry and reactivity [15,53].

ILs exhibit outstanding general properties and features, such as being relatively environmentally friendly, also, they possess good chemical and thermal stability, low vapour pressure, ability to dissolve a broad range of inorganic and organic compounds and allow simple recovery process. The characteristic of ILs as green solvents can be highlighted by their nature of having either acid or base properties, which can be modified by altering the combination of cations and anions in IL. The factors which determine the acidity of an IL are the presence of different nitrogen groups, the length of the hydrocarbon chain, and the existence of anion in the IL system [58].

The utilization of ILs in various industrial applications has progressed since their early discovery. Among them as a homogeneous catalyst in hydrogenation and hydroformylation reactions, in the removal of heavy metal traces and aromatic hydrocarbon, in protein extraction, and alkene/paraffin separation [53,56].

Besides that, when ILs are used as catalysts in biodiesel synthesis at the end of the reaction, a biphasic system is formed. In which biodiesel entirely occurs in the upper phase, and the lower phase contains the IL and glycerol with traces amount of methanol [52].

3.1 IONIC LIQUIDS APPLIED IN BIODIESEL PRODUCTION

The direct use of ionic liquids as the catalyst for the transesterification of oils to biodiesel has been much discussed in the last two decades due to their properties, and the fact of ILs catalysis could decrease the number of reactions and purification steps required

in the biodiesel preparation and separation, thus allowing for more competitive economic processing and yielding higher purity of esters [59]. Firstly, the studies carried out were related to the transesterification reaction of unused commercial oils catalysed by ionic liquids, and the majority of these studies focused on the discussion of acidic homogeneous ionic liquids' use.

Elsheikh et al. (2011) [59] prepared biodiesel via a two-step transesterification process with crude palm oil as feedstock and investigated the catalytic activity of imidazolium-containing ionic liquids, such as [BMIM]HSO_4, [BIM]HSO_4, [MIM]HSO_4. Among them, 1-butyl-3-methyl-imidazolium hydrogensulfate ([BMIM]HSO_4) was found to show the best results. The optimal conditions were reached at 160 °C, 4.4% in weight of catalyst concentration, alcohol/oil molar ratio of 12:1 and reaction time of 120 min, achieving a biodiesel yield of 91.2%. The second process was performed at a stirring speed of 600 rpm, 60 °C, 1.0% KOH for 50 minutes and the final biodiesel product achieved 98.4% yield.

Li et al. (2014) [60] investigated a microwave-assisted biodiesel production from Camptotheca acuminata seed oil catalysed by Brønsted acidic ionic liquids. Among the ionic liquids considered: 1- butyl-3-methylimidazolium bromide, [BMIM]Br; 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM]BF_4; 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4; 1-butylsulfonic-3-methylimidazolium tetrafluoroborate, [BSO_3HMIM]BF_4; 1-sulfobutyl-3-methylimidazolium hydrogen sulfate [BSO_3HMIM] HSO_4, [BSO_3HMIM] HSO_4 showed the best catalytic performance with a conversion yield of 57.8%. This acidic IL was chosen for further experiments combined with metal surfaces and [BSO_3HMIM] HSO_4–$Fe_2(SO_4)_3$. A high conversion yield of 95.7% was achieved in about 60 minutes under a temperature of 60 °C, a catalyst dosage of 4%, and a methanol/oil molar ratio of 5:1 was chosen as the optimal.

The use of waste cooking oil instead of unused oil as a raw material for biodiesel production is a substantial way, not only to reduce the high cost of biodiesel but to solve the waste-disposal problem as well [61]. In this respect, studies involving the use of ionic liquids as catalysts for the transesterification of waste cooking oils began to be carried out.

Han et al. (2009) [62] prepared a Brønsted acidic ionic liquid with an alkane sulfonic acid group as a catalyst in the synthesis of biodiesel from waste oils. When the molar ratio of methanol:oil:IL was 12:1:0.06, the yield of fatty acid methyl esters could

reach 93.5% after the reaction of acidic oil with methanol had taken place at 170 °C for 4 hours.

The production of biodiesel from waste palm cooking oil using an acidic ionic liquid as a catalyst was conducted by Ullah et al. (2015) [11] through a two-step process. In the first part of the process, waste cooking oil and methanol went through an esterification reaction catalysed by an ionic liquid to decrease the acidity of the oil. The second part consisted of a transesterification reaction in which KOH was used as a catalyst. Among the three ionic liquids used in the first phase of the process, 1-butyl-3-methylimidazolium hydrogen sulfate [BMIM]HSO_4; butylimidazolium hydrogen sulfate [BIM]HSO_4 and methylimidazolium hydrogen sulfate [MIM]HSO_4, [BMIM]HSO_4 was the most effective. Its use reduced the WCO acid value to lower than 1.0 mg $KOH.g^{-1}$, and the highest biodiesel yield was obtained with 5 wt.% $BMIMHSO_4$, molar ratio methanol:oil of 15:1, a reaction time of 60 minutes, at 160 °C, and stirring speed of 600 rpm. At the end of the process, the overall yield reached was 95.65%.

Ullah et al. (2017) [61] prepared four dual-functionalized Brønsted acids based ILs with different anions and applied as catalysts for biodiesel synthesis from waste palm cooking oil. The optimized conditions for the biodiesel production from WCO with the IL 3-methyl-1-(4-sulfo-butyl)-benzimidazolium trifluoromethanesulfonate [BSMBIM][CF_3SO_3] were catalyst concentration 4 wt.%, methanol to oil molar ratio of 12:1, temperature, 120 °C, stirring speed, 700 rpm, and time of 4 hours.

Basic ILs are also used in biodiesel production, but not as frequently as acidic ILs. The most used are imidazolium-based ILs, such as imidazolium hydroxides and imidazolide, choline-based ILs such as choline hydroxide, choline methoxide, and choline imidazolium [57]. The use of acidic ionic liquids as a catalyst in biodiesel production has been a topic of interest in many studies so far, but reaction conditions including temperature and pressure are more severe in the presence of these catalysts compared to basic ionic liquids. Therefore, due to moderate reaction conditions required in the presence of basic ionic liquids, and aiming lower reaction times, it becomes interesting to study the reactions catalysed by these substances [48].

In this scenario, Liang et al. (2010) [63] synthesized five basic binuclear functional ionic liquids with an imidazolium structure via a two-step method and used them as a catalyst in biodiesel preparation through transesterification from cottonseed oil. Among the catalysts, bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide (IMC_2OH) performed best. The fraction and selectivity of fatty acid methyl ester in the biodiesel

product reached 98.5 and 99.9%, respectively, at 55 °C for 4 h with a bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide catalyst dosage of 0.4% and methanol to cottonseed oil molar ratio of 12:1.

Fan et al. (2013) [64] explored the catalytic synthesis of biodiesel from soybean oil by transesterification over basic ionic liquid catalysts, choline hydroxide (ChOH), choline methoxide (ChOMe) and choline imidazolium (ChIm) at atmospheric pressure. Among the selected ionic liquids, ChOH exhibited the best catalytic performance. The biodiesel yield reached 95.0% when the molar ratio of methanol and soybean oil was 9:1, the optimum catalyst dosage 4 wt.%, at 60 °C for 2.5 hours.

A comparative study on the catalytic activities of different basic ionic liquids and conventional basic catalysts was carried out under the same reaction conditions by Zhou et al. (2012) [65]. After being found that 1-butyl-3-methylimidazolium hydroxide, [BMIM]OH was the best ionic liquid catalyst, transesterification of glycerol trioleate was carried out over this basic ionic liquid. As an optimal reaction condition was established 120 °C for reaction temperature, 8 hours to reaction time, a ratio of methanol to glycerol trioleate of 9:1 achieving 87.2% yield of methyl ester.

In more recent studies, the use of solid basic catalysts is investigated as performed by Xie and Wan (2018) and Hosseini et al. (2019). Xie and Wan (2018) [66] prepared a magnetically separable and efficient solid base catalyst, Fe_3O_4@HKUST-1-ABILs through the immobilization of basic ABILs (amino-functionalized basic IL) on the core-shell structured magnetic Fe_3O_4@HKUST-1 composites, which was employed in the catalytic conversion of soybean oil into biodiesel. An oil conversion of 92.3% could be achieved after 3 h of reaction at 65 °C when the transesterification reaction was performed with methanol:oil molar ratio of 30:1 and a catalyst dosage of 1.2 wt.%.

Hosseini et al. (2019) [67] performed a study of a stabilized basic ionic liquid, chlorocholine hydroxide (CCH), through immobilization on boehmite nanoparticles. The desired catalyst was first synthesized and then stabilized on boehmite nanoparticles (BNPs-CCH). Variables such as weight percentage of catalyst, methanol to oil molar ratio, and reaction time were evaluated to study the catalyst efficiency in the production of biodiesel from soybean oil and methanol. Results showed that the maximum biodiesel yield was obtained in 95.2% for optimal conditions of 11:1, 4.13 wt.%, 60 °C, and 4.4 hours. Table 6 summarizes the information discussed above.

Table 6. Summary of the experimental conditions found in the literature for biodiesel production.

Reaction	Feedstock	Ionic Liquid	Molar Ratio alcohol:oil	Catalyst Dosage (wt.%)	Temperature (°C)	Reaction Time (h)	FAME content (%)	REF
Esterif.	Palm Oil	[BMIM]HSO_4	12:1	4.4	160	2	91.20	[59]
Trans.	*Camptotheca acuminata* Seed Oil	[BSO_3HMIM]HSO_4 –$Fe_2(SO_4)_3$	5:1	4	60	1	95.70	[60]
Esterif.	Waste Cooking Oil	[BMIM]OH	15:1	5	160	1	95.65	[11]
Trans.	Waste Oil	SO_3H –Brønsted acidic IL	12:1	0.06*	170	4	93.50	[62]
Trans.	Waste Cooking Oil	[BSMBIM][CF_3SO_3]	12:1	4	120	4	94.52	[61]
Trans.	Cottonseed Oil	IMC_2OH	12:1	0.4	55	4	98.50	[63]
Trans.	Soybean Oil	[BMIM]OH	9:1	4	60	2.5	95.00	[64]
Trans.	Glycerol Triolate	[BMIM]OH	9:1	-	120	8	87.20	[65]
Trans.	Soybean Oil	Fe3O4@HKUST-1-ABILs	30:1	1.2	65	3	92.30	[66]
Trans.	Soybean Oil	BNPs-CCH.	11:1	4.13	60	4.4	95.20	[67]

*molar ratio dosage.

3.2 IONIC LIQUID RECOVERY

As mentioned before, in the biodiesel production process, the catalyst used is discarded after the transesterification step, especially homogeneous catalysts. Therefore, an option to offset the drawback of the ILs' high prices compared to conventional catalysts is to reclaim the ionic liquids and recycle them for the next reaction cycle. By doing this, the disposal of ILs in the industrial application can be minimized, thus reducing its impact on the environment. Recycling methods for these components, such as extraction by supercritical carbon dioxide, distillation, physical adsorption, crystallization, and separation by membrane are being investigated [53].

Ullah et al. (2015) [11] conducted experiments for [BMIM]HSO_4 recycling to study the efficiency of recovery. After settling at room temperature, the transesterification reaction mixture was separated into three layers: the upper one was biodiesel, the middle one was glycerol, and the bottom one was IL. But in most experiments, the IL layer was not visible as it is miscible in glycerol. After separating the biodiesel layer from the mixture, the remaining sample was centrifuged, and the bottom layer (IL) was separated and washed with hexane and ethyl acetate and then dried under vacuum for 4 h. The recycled IL was then charged with methanol followed by WCO for biodiesel synthesis. The process was successfully repeated and after the sixth time of reusing this catalyst, the yield decreased to 83%.

Ullah et al. (2017) [61] studied the reusability of [BSMBIM][CF_3SO_3] IL as a catalyst at optimized reaction conditions. The IL was reused after removing the glycerol by extraction with ethyl acetate followed by centrifuge. The catalyst was used repeatedly for eight times for the conversion of WCO to biodiesel. Results showed that the catalyst could be repeatedly used for seven times with maximum yield. This high percentage indicated that the activity of the catalyst was retained after recycling. However, the biodiesel yield decreased as the number of cycles increased, and at the eighth use, the reaction yield decreased to 70.5%.

Liang et al. (2010) [63] verified that the catalytic activity only slowly declined with the increase of repeated cycles. In this study, after the reaction was concluded, the methanol in the lower phase, composed by methanol, glycerol and the catalyst, was removed at 70 °C by atmospheric distillation. The glycerol was removed at 160 °C by distillation under vacuum (400 Pa), then, the basic dicationic functional ionic liquid catalyst was vacuum dried at 40 °C for reuse in the next cycle. The percentage of FAME decreased to 96.2% after the catalyst was repeatedly used for 7 times.

To investigate the reusability of ChOH Fan et al. (2013) [64], first distilled the lower phase, which contained the IL catalyst, glycerol, and excess methanol to separate the methanol from the mixture. Then the ionic liquid was separated from glycerol by solvent extraction, and the desired IL was presented in the upper 1-butanol phase. The 1-Butanol was removed by vacuum distillation to achieve the desired ionic liquid. The recovery of the ionic liquid was above 95%. When employed for the second time, the biodiesel yield remained 90.1%, and after four successive uses, ChOH still yields 82.5%.

It is expected that insignificant changes occur in the catalytic activity of recycled IL after proper separation and purification steps. Liang et al. (2010) [63], and Ullah et al. (2017) [61] explain that the decrease in the catalytic performance of the IL during the cycles might be because of traces of glycerol not completely removed which interact with the anion of IL through possible hydrogen bonding.

3.3 IONIC LIQUIDS APPLIED IN THIS STUDY

3.3.1 Bis-(3-Methyl-1-Imidazolium-) -Ethylene Dihydroxide

Dicationic ionic liquids (DILs) are a more recent class of ILs that have attracted attention as they represent an interesting variation of the monocationic analogues in terms of properties. DILs exhibit promising potential due to the fact they show several benefits in terms of volatility and thermal stability, as well as tenability of chemical and physical properties, compared to conventional monocationic ionic liquids [68,69].

The basic ionic liquid, bis-(3-methyl-1-imidazole)-ethylene dihydroxide, denoted as IMC_2OH is demonstrated in Figure 10. The structure of the selected ionic liquid involves an imidazolium-based cation and a hydroxide anion.

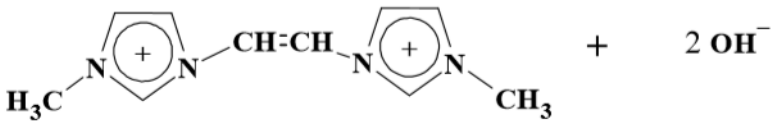

Figure 10. Structure of bis-(3-methyl-1-imidazole)-ethylene dihydroxide.
Source: Adapted from Andreani et al. (2012) [15]; Liang et al. (2010) [63].

Regarding the dicationic nature of ILs, it is reported in the literature that dicationic ILs exhibit higher values for thermal stability than monocationic ones. Shirota et al.

(2011) [70], confirmed experimentally that the decomposition temperatures (T_d) of the dicationic ILs are approximately 20 K to 40 K higher than that of the monocationic ILs. With the broader range and systematic data in the study, it was showed that it is a general nature for imidazolium-based dicationic ILs. Therefore, dicationic ILs are suitable for utilization at high-temperature conditions.

With respect to the different carbon lengths of imidazole dicationic cation, the study carried out by Zhao et al. (2013) [71] revealed that the thermal stability decreased with the increase of the alkyl carbon length. Besides that, by applying several dicationic imidazolium-based catalysts with different alkyl group length in the transesterification of cottonseed oil, Liang et al. (2010) [63] found the highest conversion value for the smallest IL chain.

Liang et al. (2010) [63] study is a successful example of an alkaline IL application in the biodiesel catalysis field, and the best results were obtained for IMC_2OH as a catalyst. IMC_2OH proved to be an efficient catalyst for the preparation of biodiesel from cottonseed oil and methanol, exhibiting a high yield of 98.5% under mild conditions.

A critical feature of the ionic liquid in terms of solubility is that bis-(3-methyl-1-imidazole)-ethylene dihydroxide presents partial or complete solubility for the reactants, yet poor solubility for the reaction products, as shown by Liang et al. (2010) [63]. Besides that, since studies showed that IL could also be distilled and vaporized for recovery purpose [53], it is assumed that IMC_2OH possess high thermal stability which means that the IL can be recovered and reused as a catalyst in the post-procedure, as investigated by Liang et al. (2010) [63] and also by Fang et al. (2013) [72]. The basic dicationic functional ionic liquid exhibited high stability upon reuse since the catalytic activity only slowly declined with the increase of repeated cycles.

3.3.2 (2-Hydroxyethyl) Trimethylammonium Hydroxide (Choline Hydroxide)

One of the strategies to design low toxicity and highly biodegradable ionic liquids is to use cations and anions based on biomolecules, such as those based on natural amino acids, lactic acid, choline, and fructose [48,73]. Choline ((2-hydroxyethyl)trimethylammonium) occurs as a cation that forms various salts, such as choline chloride, which is a water-soluble essential nutrient commonly recognized as belonging to the group of vitamin B complexes and it possesses important biological functions. It is used as a starting material for the development of biocompatible ionic

liquids since the presence of the hydroxyl group in the cation increases the biodegradability of the compound [74].

In this sense, the use of choline hydroxide (ChOH) has been considered an appropriate catalyst choice for the production of biodiesel. Compared to other ionic liquids, the synthesis of choline hydroxide involves less complexity, and its raw materials are much less expensive and are commercially available for purchase [48]. The structure of choline hydroxide is represented in Figure 11.

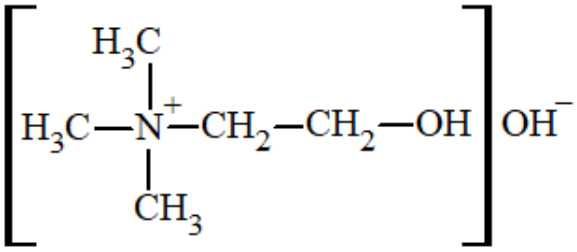

Figure 11. Structure of choline hydroxide.
Source: Fan et al. (2013) [64].

Among the studies in catalysis for the production of biodiesel, Bessa (2015) [75] carried out an experimental design to investigate the influence of the variables oil/alcohol molar ratio, temperature, and catalyst concentration in the conversion of triacylglycerols and FFA into methyl esters from WCO. From the evaluation of the operational conditions, optimum conditions found were 1:12 oil/methanol molar ratio, 5.5 wt.% of catalyst, 40 °C, and 3 hours of reaction.

Fan et al. (2013) [64] evaluated the synthesis of biodiesel from soybean oil by transesterification. From the operational conditions employed of oil/methanol molar ratio of 1:6, 1:9, 1:12, 1:15, and 1:18, catalyst concentration of 1%, 2%, 4%, 6%, 8%, and 10%, and temperature of 30, 40, 50, 60 and 65 °C, ChOH showed better catalytic performance when a 1:9 molar ratio of soybean oil/methanol was applied, a catalyst dosage of about 4% by weight, at 60 °C and 2,5 h.

Anjos (2018) [76] optimized the biodiesel catalysis parameters from soybean oil. The following operational process parameters were evaluated: temperature (50, 60, 70 and 80 ºC), oil/alcohol molar ratio (1:6, 1:9, 1:12 and 1:15) and catalyst dosage (5%, 10% and 20% (w/w)). For ChOH, the best operational conditions were a temperature of 70 ºC, 1:15 molar ratio of oil/alcohol, 10% (w/w) of catalyst, and 3 hours of reaction, obtaining 94% of methyl esters.

Gholami et al. (2019) [48] assessed the potential of biodiesel production from Norouzak oil using ChOH in a microchannel reactor. The highest reaction efficiency was 93.36% at a catalyst concentration of 6.11 wt.%, oil/methanol molar ratio of 1:8.8, and a reaction time of 12.48 min. In order to assess the model accuracy, an experiment was conducted at the optimal point predicted by the model, and it was obtained a biodiesel production efficiency of 96.8%. An interesting conclusion of the authors was that, when choline hydroxide is used instead of heterogeneous catalysts in microchannel reactors, in order to obtain shorter reaction times, smaller amounts of catalyst and alcohol are needed to achieve efficiencies higher than 90%. According to Gholami et al. (2019) [48], the amount of catalyst and alcohol used in the study were, respectively, 0.72-0.77 and 0.37-0.70 of those in the presence of heterogeneous catalysts, suggesting that choline hydroxide has a high potential to be used in reactions of transesterification.

3.4 KINETIC STUDY

The primary interest in the operation of chemical reactions is to have knowledge and understanding of chemical kinetics. It is important to perform kinetic modelling to determine the activation energy since it is linked to overcoming an energy barrier between reactant molecules and some transition, which is inherent for each reaction and is a significant parameter for the selection and design of biodiesel production [77–79]. In cases that the reaction presents small activation energy, it is poorly sensitive to the temperature. Unlike reactions with a high activation energies value, there is a strong dependency on temperature [79,80].

An option to increase the rate of the desired reaction is to apply a catalyst since it provides a different pathway for a chemical reaction. They do not appear in the overall stoichiometry of the reaction and are not used during the reaction [78].

There are studies in the literature that focuses on the estimation of the activation energy, although the literature on kinetic modelling using WCO with the conventional method for biodiesel production are a few [77]. Some of these studies are summarized in Table 7.

Table 7. Review of kinetic studies for transesterification to biodiesel synthesis.

Feedstock	Catalyst	Alcohol	Temperature Range (°C)	Order	Activation Energy ($KJ.mol^{-1}$)	REF
WCO	NaOH	Methanol	50	1^{st}	88.76	[81]
C. acuminata seed oil	$[BSO_3HMIM]HSO_4–Fe_2(SO_4)_3$	Methanol	40-60	1^{st}	37.68	[60]
WCO	$[BSMBIM][CF_3SO_3]$	Methanol	80-140	1^{st}	19.24	[61]
Cottonseed WCO	KOH	Methanol	45-55	pseudo-1^{st}	13.05[A]	[77]
Cottonseed WCO	CaO	Methanol	45-55	pseudo-1^{st}	28.93[B]	[77]
Cottonseed WCO	KOH	Methanol	45-55	pseudo-1^{st}	34.5[C]	[77]
Cottonseed WCO	CaO	Methanol	45-55	pseudo-1^{st}	50.4[D]	[77]
Palm oil	NaOH	Methanol	60. 70	2^{nd}	-	[82]
Jatropha oil	KOH	Methanol	45	2^{nd}	-	[83]

A,B - microwave-assisted transesterification process; C,D - conventional transesterification method

Jain et al. (2011) [81] studied the kinetics of base-catalysed transesterification process of waste cooking oil under optimum conditions of methanol to oil ratio of 3:7 (v/v), temperature of 50 °C, and catalyst concentration of 1 wt.% of NaOH. The results indicated that transesterification reaction was of first-order rate reaction with reaction rate constant of 0.0078 min^{-1}, and the activation energy for transesterification of WCO was 88.76 $kJ.mol^{-1}$.

Li et al. (2014) [60] conducted microwave-assisted biodiesel production with *C. acuminata* seed oil and a Brönsted–Lewis acidic IL, $[BSO_3HMIM]HSO_4–Fe_2(SO_4)_3$. A detailed study on the kinetic behavior was carried out to temperatures ranged from 40 to 60 °C. An Arrhenius plot of the conversion process confirmed that it was a first-order reaction in the studied temperature range, and it was found activation energy of 37.68 $kJ.mol^{-1}$, and reaction rate constant for 40, 50, and 60 °C of 0.0092, 0.0124, and 0.0217 min^{-1}, respectively.

In the studies carried out by Ullah et al. (2017) [61] the transesterification of waste palm cooking oil with the IL 3-methyl-1-(4-sulfo-butyl)-benzimidazolium trifluoromethanesulfonate $[BSMBIM][CF_3SO_3]$ was investigated. The biodiesel

production was studied at four different temperatures to determine the value of the activation energy, which was 19.24 $kJ.mol^{-1}$, and a first-order kinetics' model proved to be the best one for this transesterification study.

Sharma et al. (2019) [77] focused on process optimization and kinetic study of microwave-assisted transesterification process using KOH and CaO catalyst from waste cotton-seed cooking oil. Experiments were performed using the optimized parameters which were for KOH methanol to oil ratio of 7:1, catalyst loading 0.65 (w/w) %, and reaction time of 9.6 minutes, and for CaO catalysed condition, the optimum values were 9.6:1, 1.33 (w/w) % and 9.7 min, respectively. It was found that by increasing the temperature from 45° to 55 °C, the reaction rate constant for transesterification reaction was found to increase from 0.2924 to 0.3401 min^{-1} for KOH catalyst and from 0.1813 to 0.2532 min^{-1} for CaO catalyst condition. The activation energy was calculated for microwave-assisted transesterification assuming pseudo-first-order reaction kinetics for both catalysts, which was found to be 13.05 and 28.93 $kJ.mol^{-1}$ for KOH and CaO respectively. In this research, the experiments were also conducted in the conventional method to verify the reaction kinetic, and the values found for KOH and CaO were 34.5 and 50.4 $kJ.mol^{-1}$, respectively.

Studies by Foon et al. (2004) [82] and Kumar et al. (2011) [83] have reported that the data from transesterification could be described reasonably by a second-order rate expression. Foon et al. (2004) verified a fast formation of palm oil methyl esters with a rate constant of 0.163 $L.mol^{-1}.min^{-1}$ when the reaction parameters applied were a molar ratio of oil to methanol of 1:10; KOH catalyst concentration of 0.125 $mol.kg^{-1}$ oil at 60 °C.

Kumar et al. (2011) investigated the transesterification of jatropha oil using methanol and 1 wt.% KOH as the catalyst. It was observed that in 30 minutes, the reaction had achieved almost complete conversion for jatropha oil at 45 °C. The best fit was found to be a second-order model exhibiting a rate constant of 1.26 $L^2.mol^{-2}.min^{-1}$.

3.5 REVIEW OF PREVIOUS WORKS

The following is 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.

Tadevosyan (2017) [84] analysed the influence of several ionic liquids as catalysts in the esterification reaction of OA. Among five ILs, [BMIM][HSO_4], [BMIM][CH_3SO_3],

[BMIM][CH_3SO_4], [MIM][HSO_4], and tributylmethylammonium methyl sulfate. The values obtained for the conversion for the esterification reaction showed that the ionic liquid [BMIM][HSO_4] was the most promising one. From this result, the recovery of the IL was studied, and several esterification reactions of oleic acid were carried out using a catalyst dosage of 10 wt.%, 15 wt.%, and 20 wt.% relative to the mass of OA. The parameters used for the reactions were: reaction temperature of 90 °C, a reaction time of 6 hours, and an oil/MeOH molar ratio of 1:10. It was verified that with the increase of catalyst amount used in the reactions, there was an increase in the percentage of FAME obtained so that, the best amount of catalyst applied to the system was 20%. In the first reaction, a conversion of 84.90% was obtained, and by the fifth cycle, it was obtained 77.10%.

Yordanova (2016) [85] studied the optimization of the esterification reaction conditions of OA using [BMIM]HSO_4, and 1-butyl-3-methylimidazolium methanesulfonate ([BMIM]CH_3SO_3). The optimal conditions found for IL [BMIM]HSO_4 were 4 hours, 110 °C, 1:10 OA/MeOH molar ratio, and 10 wt.% catalyst dosage. Regarding the ionic liquid [BMIM]CH_3SO_3, it was reported that there were no results in the esterification performed in the presence of this catalyst.

Alimova (2016) [86] evaluated the effect of different operating parameters in the esterification of oleic acid with methanol into biodiesel with an acidic IL, [BMIM][HSO_4]. The optimum conditions for the esterification were identified as an OA/MeOH molar ratio of 1:10, a catalyst amount of 10 wt.%, a reaction time of 4 h, and a reaction temperature of 90 °C.

Goes (2018) [87] studied the influence of the application of [HMIM]HSO_4 in the catalysis of the transesterification reaction of the triacylglycerol mixtures present in a simulated oil through the incorporation of oleic acid in a WCO. The optimum reaction conditions for the conversion response were a reaction time of 8 h, 1:40 oil/MeOH molar ratio, 20% OA incorporation, temperature of 90 °C and catalyst dosage of 10 wt.% achieving an average conversion of 96.60%. For FAME response it was: 40 % OA incorporation, 8 h, 1:20 oil/MeOH molar ratio, 90 °C, and 10 wt.% catalyst dosage obtaining a conversion of 36.50%. Also, the recovery and reuse of the IL were carried out of five consecutive experiments. A decreasing conversion rate was achieved throughout the measurements, more than 85%, while the FAME content remained near an average of 35% in the first four experiments and dropped to 30% in the fifth recover experiment. Besides that, a study to promote the transesterification reaction of the WCO was conducted using the IL and NaOH simultaneously. However, all reactions showed high

conversion rates, 90%, and low FAME contents, less than 1%, which indicated that only the saponification with NaOH and esterification by IL occurred.

Meireles (2018) [88] aimed to evaluate [BMIM][MeSO4] IL as a catalyst for the esterification process of oleic acid with methanol. The study showed the highest conversion of 92.4% for the following operational conditions: 10 wt.% of catalyst load, molar ratio of 1:10 OA/MeOH, a reaction time of 8 hours, at 65 °C. In order to determine the order of the esterification reaction, a study was carried out using 10% wt. of catalyst, OA/MeOH molar ratio of 1:6 for 4 hours, for the temperatures of 45.50 and 65 ℃. The parameters for the kinetic study were estimated as 57.9 kJ/mol for the activation energy, and a pre-exponential factor of 0.0448 $L.mol^{-1}.min^{-1}$. The recovery of the ionic liquid was tested using three different methods: drying, rotary evaporator, and washing with different solvents. The application of the various processes in the recovery of the IL showed a very low correlation, which shows that the recovered IL contains unknown impurities. The purity of the recovered IL was verified through FTIR analysis, for the samples of IL at 20% (w /w), demonstrating a correlation of 96%. Thus, because it is an acid-catalysed esterification, and the IL is hydrophilic, the best recovery method performed was using water in the washing process.

Roman (2019) [89] studied the esterification reaction of oleic acid with methanol, also with $[HMIM]HSO_4$, as a catalyst. The optimum conditions for the conversion were determined as 8 h, 110 °C, OA/MeOH molar ratio of 1:15 and a catalyst dosage of 15 wt.%, resulting in a conversion of 95%, and for the FAME content were 8 h, 110 °C, OA/MeOH molar ratio of 1:14 and a catalysts dosage of 13.5 wt.%, leading to a content of 90%. The kinetic experiment was carried out using the best conditions for the conversion for a temperature range varied from 70 °C to 110 °C. The results were well described using a third-order reaction model, and it was found an activation energy of 6.8 kJ/mol and a pre-exponential factor of 0.0765 $L^2.mol^{-2}.min^{-1}$.

Baú (2019) [90] explored the esterification reaction of a simulated oil by the incorporation of oleic acid (OA) into the waste cooking oil and the $[BMIM]HSO_4$ IL. In this study, the best conditions for conversion using the simulated oil with a catalyst load of 10 wt.% and a reaction temperature of 65 °C was the incorporation of OA of 20 wt.% , a reaction time of 8 hours, and an oil/MeOH molar ratio of 1:20. For the FAME content, the optimum condition was similar to the one mentioned above, with the differential for the incorporation of OA of 40 wt.%. For determination of the activation energy value, reaction tests were carried out with the temperatures of 45, 50, 55, 60, and 65 °C. The kinetic studies showed that the esterification reaction of oleic acid could be modelled as

a third-order reaction with an activation energy of 52.20 $kJ.mol^{-1}$, and it was significantly influenced by the temperature and molar ratio of oil/alcohol. Besides that, the acidic IL was recovered and reused for five reactions/recovery cycles. It was found that the conversion efficiency dropped from 93.4% to 86.9% and the content of FAME decreased from 18.4% by weight to 11.5%.

Belhaj (2019) [91] studied the performance of $[HMIM]HSO_4$ catalyst using different amounts of the IL (10%, 15%, and 20%) in the esterification of oleic acid and methanol, for the conditions of 1:10 oil/MeOH molar ratio, a reaction time of 4 hours, and reaction temperature of 65 °C. Among the reactions for each amount of catalyst, the highest conversion was found for the catalyst dosage of 15%. Two methods for drying the aqueous samples (lower phase of biodiesel production through esterification) were applied for the recovery of the IL. The first one implied the drying of the sample in an oven at 110°C, and the other one was a drying process in a vacuum oven at 60°C/70 °C. From the application of the recovered IL in new reaction cycles, the highest conversions were obtained with an amount of catalyst of 20%, which after 4 cycles was 59.39%.

A summary of what was exposed is presented in Table 8.

Table 8. Summary of preview works done by the research group.

Work	Tadevosyan	Yordanova	Alimova	Goes	Meireles	Roman	Baú	Belhaj
Reaction Type	Esterif.	Esterif.	Esterif.	Esterif.	Esterif.	Esterif.	Esterif.	Esterif.
Feedstock	OA	OA	OA	WCO/OA	OA	OA	WCO/OA	OA
Ionic Liquid	[BMIM]HSO_4	[BMIM]HSO_4	[BMIM]HSO_4	[HMIM]HSO_4	[BMIM][$MeSO_4$]	[HMIM]HSO_4	[BMIM]HSO_4	[HMIM]HSO_4
Oil/MeOH Molar Ratio	1:10	1:10	1:10	1:40	1:10	1:15	1:20	1:10
Catalyst Dosage (wt.%)	20	10	10	20	10	15	20	15
Temp. (°C)	90	110	90	90	65	110	65	65
Reaction Time (h)	6	4	4	8	8	8	8	4
Conversion (%)	84.90	85.88	89.70	96.60	92.40	95.00	87.80	91.26
Activation energy (kJ/mol)	-	-	-	-	57.90	6.80	52.20	-
Pre-exponential factor	-	-	-	-	0.0448 $L.mol^{1}.min^{-1}$	0.0765 $L^2.mol^{-2}.min^{-1}$	$2.46.10^3$ $L^2.mol^{-2}.min^{-1}$	-
REF	[84]	[85]	[86]	[87]	[88]	[89]	[90]	[91]

4. TECHNICAL DESCRIPTION AND PROCEDURES

4.1 CHEMICALS AND RAW MATERIALS

The reactants used for the synthesis of the ionic liquid bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide (IMC_2OH), 1,2-dibromoethane, sodium hydroxide, and dichloromethane were purchased from Sigma Aldrich, the acetone and acetonitrile were purchased from Riedel-de-Haën, and the N-methyl-imidazole was obtained from Tokyo Chemical. For the transesterification with choline hydroxide, the IL was purchased from Sigma Aldrich, methanol from Riedel-de-Haën, sunflower oil from Vita 'Dor, and waste cooking oil, from restaurants in the region of Bragança, Portugal.

The materials utilized for characterization and analysis were n-heptane (99%), and sodium sulfate anhydrous purchased from Carlo Erba. Diethyl ether, borax, and red methyl indicator were obtained by Riedel-de-Haën. Concentrated sulfuric acid, 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%), butanol, and sodium chloride were obtained by Panreac. Ethyl acetate was obtained from Labscan.

4.2 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). The samples masses were measured with an analytical balance with a precision of ±0.0002 g (AE, model ADA 210/C). Furthermore, the FAMEs content in biodiesel samples was evaluated in a gas chromatograph system chromatograph (SHIMADZU Nexis GC-2030) equipped with an FID detector, an autoinjector AOC- 20i, and an OPTIMA BioDiesel F (30mx0.25mmx0.23µm) capillary column. For infra-red spectroscopy, a PerkinElmer spectrometer, model Spectrum Two FT-IR with a Universal ATR accessory was used. For the purification of the ionic liquids, a rotary evaporator Büchi Labortechnik AG, and a vacuum oven from Lab-Line Instruments were used. For the study of ChOH recovery, the vortex Reax Top from Heidolph was used.

4.3 METHODOLOGY

4.3.1 Procedure for the Synthesis of IMC2OH Ionic Liquid

The ionic liquid synthesis consists of a two-step procedure as described by Liang et al. (2010) [63]. In the first step, it was prepared an intermediate, called bis-(3-methyl-1-imidazole)-ethylene dibromosalt by stirring 1,2-dibromoethane and dehydrated N-methyl-imidazole in an acetonitrile solution in a flask at 70 °C for 24 hours. After that, the mixture was cooled down to room temperature and filtered to give a crude solid. This solid was washed three times with 30 mL of acetone, and then the solvent was evaporated in an oven at 70 °C. In the second step, the solid bis-(3-methyl-1-imidazole)-ethylene dibromosalt and NaOH were dissolved with acetone in a single-neck flask and stirred at room temperature for 24 hours. In addition to that, the resulting precipitate of sodium bromide was filtrated, washed with acetone to ensure that only NaBr remained in the solid, and the solvent was evaporated under vacuum in a rotary evaporator. The acquired mixture is agitated with dichloromethane and left to decant in a separating funnel until it can be visualized two phases. The phases were separated, and the solvent was evaporated under reduced pressure to yield bis-(3-methyl-1-imidazole)-ethylene dihydroxide. The scheme of the process of synthesis is presented in Figure 12.

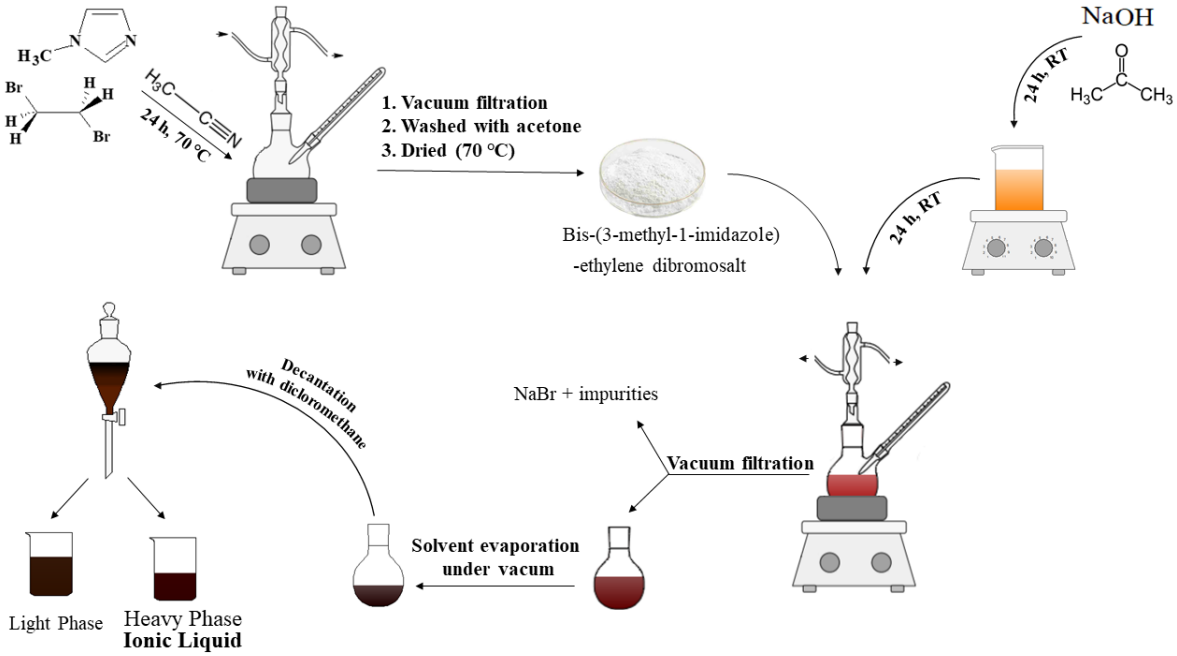

Figure 12. Scheme for the synthesis of bis-(3-methyl-1-imidazole)-ethylene dihydroxide.

4.3.2 Transesterification Reaction of Sunflower Oil

The required amount of oil was taken into a 100 mL two-necked reaction flask. The ionic liquid was weighed, and methanol was also added into it. Subsequently, the reaction flask was immersed in a paraffin bath (1), which was coupled with a reflux condenser (2) and placed over an automatic heating plate with agitation (3) and automatic temperature control. The mixture was heated to the desired temperature, and thereafter the reaction time count was started. An extra thermometer (4) was used to confirm the temperature inside the reaction flask, as shown in Figure 13.

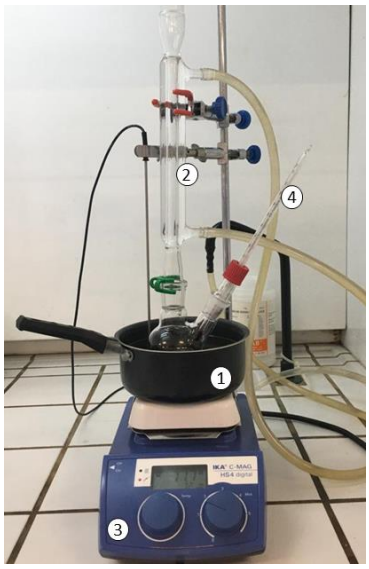

Figure 13. Experimental apparatus for the transesterification reaction.

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.

4.3.3 Acidity Measurement

The acid value was determined to measure the degree of occurrence of free fatty acids (FFAs) present in oils used in the study, and the calculation was performed following EN 14104 Standard [92]. 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 1:1 (v/v) ethanol/diethyl ether and 5 drops of phenolphthalein was added into the flask. Then, the solution was titrated with a standard solution of potassium hydroxide. The acid value is given in terms of mg of KOH/g sample by Equation 1.

$$AV = \frac{V_{KOH} * C_{KOH} * MW_{KOH}}{m_{Sample}} \quad (1)$$

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.

4.4 CHARACTERIZATION OF BIODIESEL

4.4.1 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 [92]. This analytical technique provides the distribution area corresponding to each component present in the sample. Figure 14 shows the equipment used to perform these analyses.

Figure 14. GC-FID equipment used for FAME content analysis in biodiesel samples.

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 10 $mg.mL^{-1}$ 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 for 3 min. 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 the same 37 FAME compound mixture supplied by Supelco using an Omegawax ™ 250 column, shown in Figure 15 [93]. 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 [94] (see Figure 16). The chromatogram obtained from the 37 FAME compound mixture in this work is presented in Figure 17.

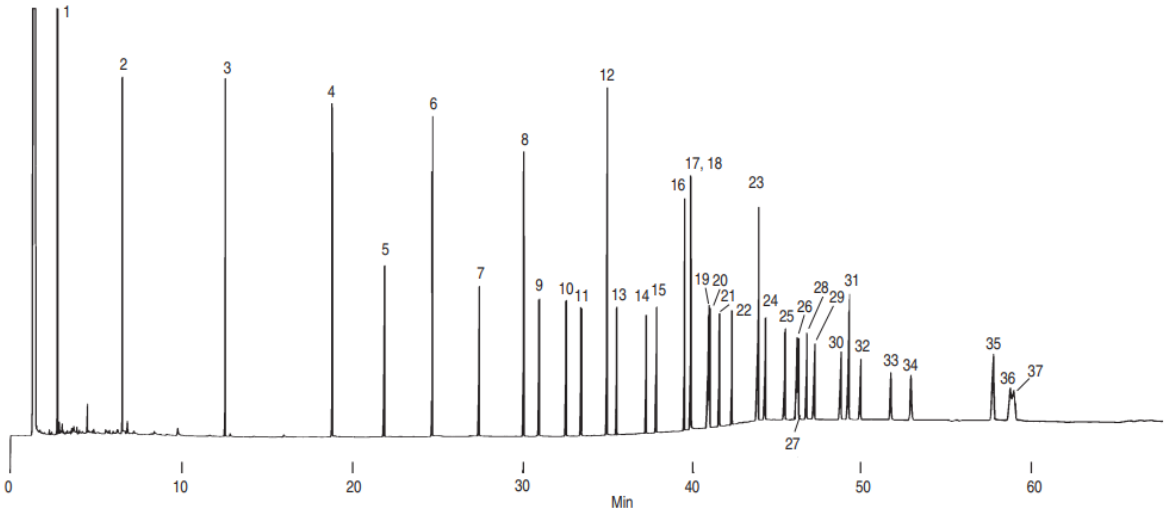

Figure 15. Chromatographic analysis obtained for the Supelco 37 Component FAME Mix on the Omegawax 250 column.
Source: Adapted from Supelco [93].

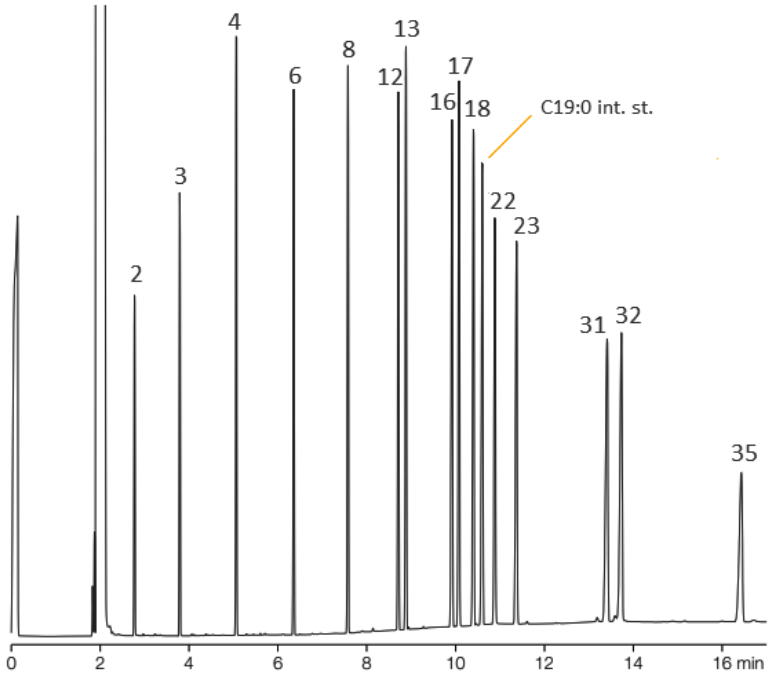

Figure 16. Chromatographic analysis obtained for a 16 component FAME mix on OPTIMA BioDiesel F column.
Source: Adapted from MACHEREY-NAGEL [94].

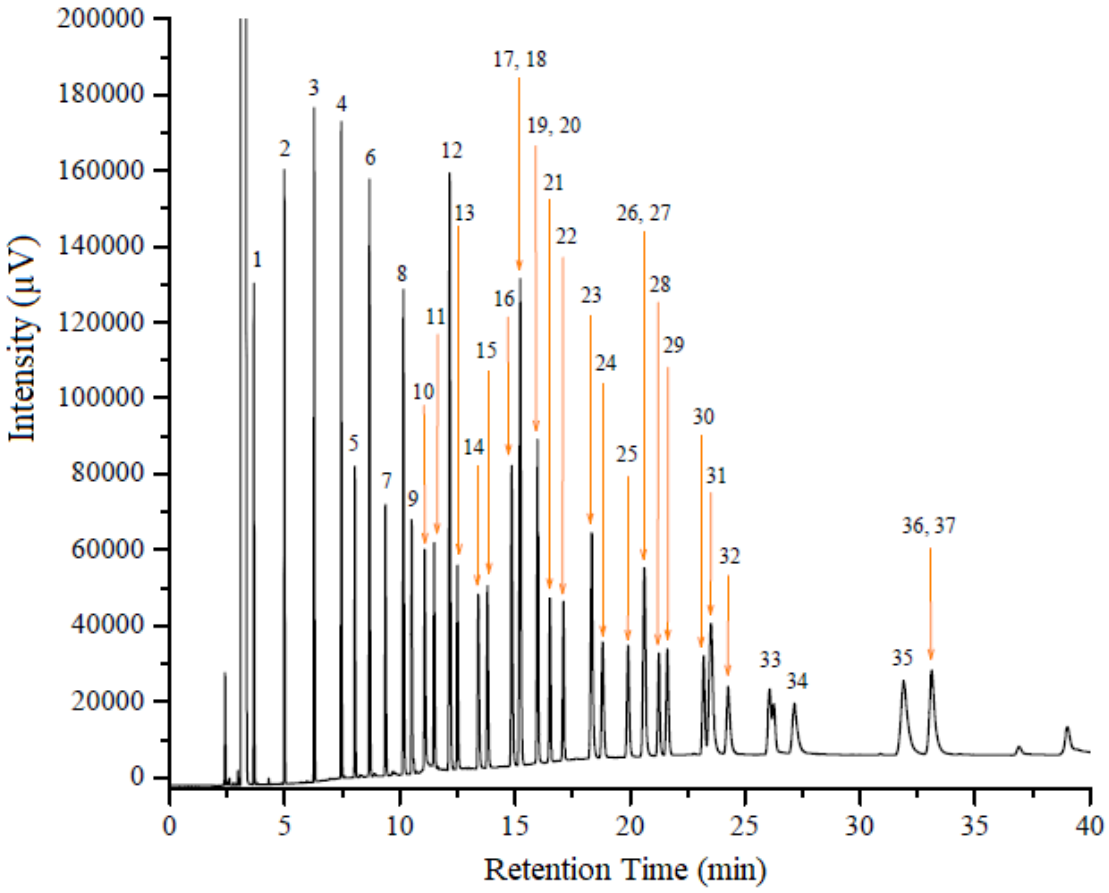

Figure 17. Chromatographic analysis obtained for the 37 compound FAME mix using the Shimadzu equipment with an OPTIMA BioDiesel F column.

Table 9 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 17. 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.

Table 9. 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

The percentage of FAME content was calculated using Equation 2.

$$C(\%) = \frac{\sum A_{FAMEs} - A_{IS}}{A_{IS}} * \frac{C_{IS} * V_{IS}}{m_{biodiesel}} * 100 \quad (2)$$

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 9. 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.

4.4.1.1 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, 500 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 10 $mg.mL^{-1}$.

4.4.1.2 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 [95]. 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. 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 in the solution, 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 mL of 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.

4.5 FT-IR ANALYSIS

FT-IR analyses were performed for several samples, from reagents to products, to analyse the compounds present in the samples by identifying each functional group vibration. FT-IR spectra were recorded using a Fourier transform infrared spectrophotometer, operating from 400 to 4500 cm^{-1} in a resolution of 4 cm^{-1} and 4 cumulative scans.

4.6 KINETIC STUDY

From the results obtained in a preliminary study, the experimental condition of catalyst dosage was selected to evaluate the reaction kinetics. With regard to the parameters of reaction temperature and alcohol/oil molar ratio, 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 0, 10, 20, 30, 45, 60, 120, 240, 360, and 480 minutes for the temperature of 65 °C.

The procedure was similar to the reaction procedure presented in Section 4.3.2. 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 amount of reagents, it was decided to carry out a reaction for each defined planning time.

4.7 STUDY OF ChOH IONIC LIQUID RECOVERY

4.7.1 Butanol/Water Solvent Extraction

Studies have been carried out to develop methods of recovering the choline hydroxide ionic liquid. First, a similar method described by Fan et al. (2013) [64] was performed. To purify the catalyst, a separation by solvent extraction with butanol and water was performed. For this study, tests were carried out in which a volume ratio of 1:1 water/butanol was maintained fixed, and the mass ratio of the water/butanol mixture and the amount of the lower phase rich in glycerol and catalyst (named catalyst phase) was varied from 1:1 to 1:6. The separation procedures consisted primarily of drying the lower phase at 110 °C to evaporate the excess of methanol. After that, the catalyst phase was measured in a test tube, and the corresponding amount of water and butanol was added. For complete mixing, the system was stirred using a vortex apparatus. Then, the mixture was left to stand until complete phase separation.

Micropipettes were used to separate the phases, and the flask containing the lower phase with glycerol, water and possible traces of IL was placed in an oven at 110 ° C, and the upper phase containing ionic liquid and 1-butanol was placed in a round bottom flask in a rotary evaporator at 130 mbar and 40 °C in order to gain the desired ionic liquid. At the end of this procedure, all samples of the upper phase were analysed by FT-IR.

4.7.2 Ethyl Acetate/Water Solvent Extraction

In addition to the tests with butanol and water, a study of solvent extraction with ethyl acetate and water was carried out the same way as described previously. In these separation tests, the volume ratio of the mixture of water/ethyl acetate was 1:1, and the mass ratio of catalyst phase/ mixture of solvents applied was 1:1, 1:2, and 1:4. For the separation of the formed phases, the lower phase supposed to contain glycerol and water and the upper phase containing the ionic liquid and ethyl acetate were separated into flasks of 4 mL and placed in the oven at 110 °C. After solvent evaporation, FT-IR analysis was performed.

5. RESULTS AND DISCUSSIONS

5.1 SYNTHESIS OF IMC_2OH IONIC LIQUID

The synthesis of the ionic liquid was performed three times, the first being a preliminary test. At the end of this synthesis, a dark brown material with a viscous consistency was obtained, differently from that reported by Liang et al. (2010) [63], which obtained a pale yellow powder. In addition, it was observed that, when washing the product with dichloromethane, only one phase was obtained, which was not expected, since the purpose of the washing at the end of the process was to remove the impurities from the material.

In the following two syntheses, the amount of the limiting reactant was tripled in order to produce a greater amount of IMC_2OH and to achieve a purer and more faithful product to that of the literature. In the dichloromethane washing step, two phases could be seen, one with a slightly lighter color and turbid and the other one more limpid and darker, as can be seen in Figure 18.

Figure 18. Appearance obtained from the washing with dichloromethane.

Also, a difficulty found in the synthesis was the fact that NaOH is not soluble in acetone, which was also not expected since no inconvenience with the synthesis was reported by the study used as a guideline. As a result, the conversions obtained in the second synthesis stage were very low, as can be seen in Table 11. Liang et al. (2010) [63] reported that it was obtained a conversion of 80% in the first stage, and for the second one was not commented on. In this referred work, the performance of IMC_2OH for the

catalysis of cottonseed oil for the production of biodiesel under the molar ratio of methanol to oil of 12:1, catalyst dosage of 0.5%, 60 °C, and reaction time of 5 h was defined as excellent, reaching 98% of FAME content.

The conversion values shown in Tables 10 and 11 were calculated by dividing the mass obtained from the intermediate/IMC_2OH by the mass that should have been obtained from the molar balance using the reaction stoichiometry, multiplied by 100.

Table 10. Data from stage 1 of IMC_2OH synthesis.

Assay	Experimental Values				Conversion
	Dibromoethane (g)	N-Methylimidazole (g)	Acetonitrile (mL)	Intermediate (g)	(%)
IL1	3.7532	3.3063	50.50	4.5974	64.87
IL2	11.20	9.70	148.00	11.9785	57.62
IL3	10.64	9.30	142.00	11.97	60.06

Table 11. Data from stage 2 of IMC_2OH synthesis.

	Experimental Values				Conversion
Assay	NaOH (g)	Acetone (mL)	IMC_2OH (g)	NaBr (g)	(%)
IL1	1.1275	65.50	1.5891	3.8014	64.04
IL2	2.9188	170.50	10.31	1.3164	17.25
IL3	5.60	170.50	16.46	2.4039	31.45

Figure 19 shows the FT-IR spectrum of the two phases obtained from the ionic liquid produced, which structure is presented earlier in Figure 10. The broad peaks at 3396 cm^{-1} and 3407 cm^{-1} are assigned to O-H stretching vibrations, which occur in the region between 3400-3200 cm^{-1}. For methyl groups, the bands at 2972 cm^{-1} and 2918 involve CH_3 stretch, and the bands near 1362 cm^{-1} involve the CH_3 in-phase deformation. The characteristic band of the spectrum in 1699 cm^{-1} can be ascribed to C=C and C=N stretch. Indeed, C=N peak may be overlapping C=C, since C=C is a weak absorption near 1650 cm^{-1}, and although the C=N band varies in intensity from compound to compound it usually is more intense than that obtained from C=C bond. The band cluster around 1179 cm^{-1} may involve the imidazole ring in-phase breathing mode [96]. Besides that, C-N stretching absorption also occurs in this region, of 1350 to 1000 cm^{-1}.

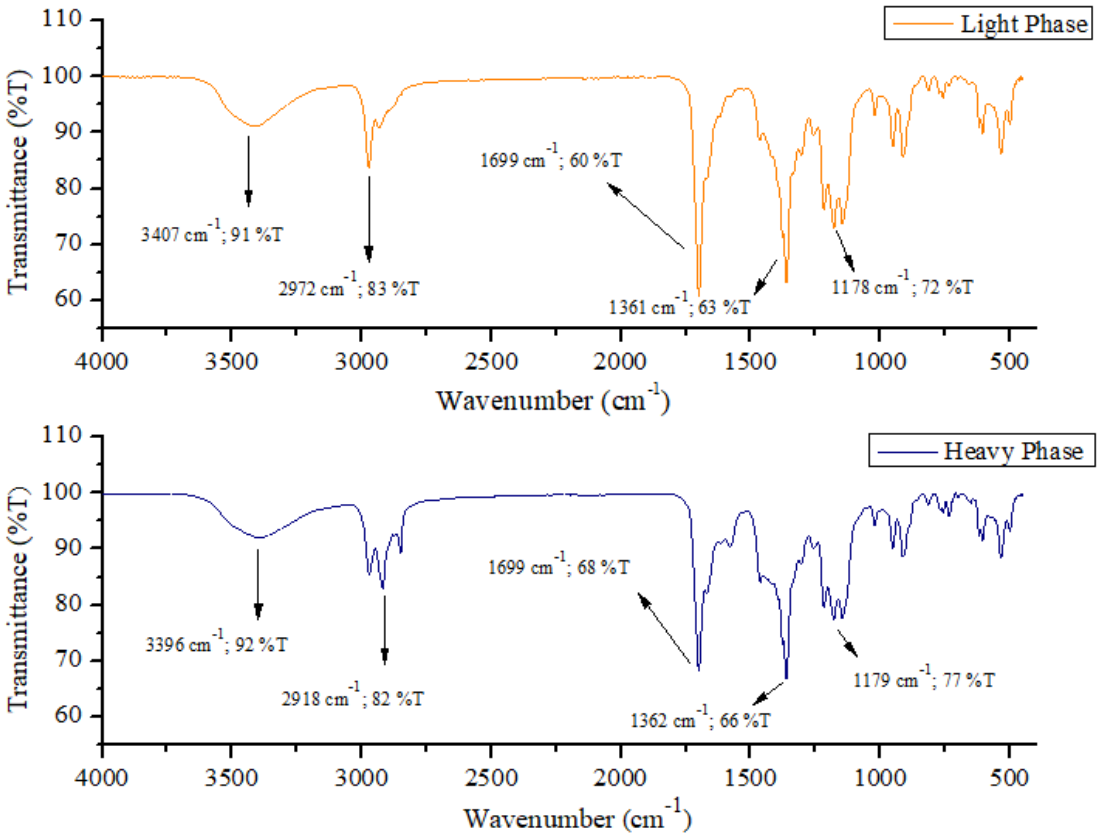

Figure 19. FT-IR spectrum of the obtained IL bis-(3-methyl-1-imidazole)-ethylene dihydroxide.

As can be seen above, the spectra of both phases are incredibly similar, which raises doubts about the separation that has occurred, and whether it is profitable.

Techniques such as NMR spectroscopy could be applied to obtain complete information about the chemical structure of the material produced. However, it was decided to proceed with other works since the development of the synthesis of this IL and the purification processes required about two weeks to be completed. Besides that, given the timeframe for the development of the work, it was not feasible to study the optimization of the process. Which could be the verification of alkylation of N-methyl imidazole under an inert atmosphere [97,98], and the investigation of a better solvent for the second stage of synthesis.

5.2 FEEDSTOCK CHARACTERIZATION

Sunflower oil (SFO) and waste cooking oil (WCO) were 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. Also, FT-IR analyzes were performed for both oils, as well as their acid values had been determined (Section 4.3.3).

GC analysis showed that saturated palmitic acid (C16:0), monounsaturated oleic acid (C18:1), and polyunsaturated linoleic acid (C18:2) were the major chemical components, as can be seen in Table 12 and 13, for SFO and WCO, respectively.

Table 12. Percentage of fatty acids identified as methyl esters of triacylglycerols in sunflower oil.

Compound Name	Compound ID	%FAME			Average (%)
		Sample 1	Sample 2	Sample 3	
Palmitic acid	C16:0	5.91	6.15	5.84	5.97
Stearic acid	C18:0	2.96	3.22	3.15	3.11
Oleic acid, Elaidic acid	C18:1 (c+t)	35.49	39.57	41.76	38.94
Linoleic acid, Linolelaidic acid	C18:2 (c+t)	48.17	50.55	48.09	48.94
Total		**92.53**	**99.49**	**98.84**	**96.95**

Table 13. Percentage of fatty acids identified as methyl esters of triacylglycerols in cooking oil.

Compound Name	Compound ID	%FAME		Average (%)
		Sample 1	Sample 2	
Palmitic acid	C16:0	8.38	8.69	8.54
Stearic acid	C18:0	3.19	3.28	3.24
Oleic acid, Elaidic acid	C18:1 (c+t)	26.86	27.50	27.18
Linoleic acid, Linolelaidic acid	C18:2 (c+t)	40.50	38.41	39.46
Linolenic acid	C18:3n3	-	2.16	2.16
Total		**78.93**	**80.04**	**80.57**

The chemical and physical properties of the raw material are directly associated with the technology and the yield of the conversion process. In addition, the fuel properties of biodiesel are influenced by its fatty acids content, which may cause differences in the characteristics of injection, combustion, and emissions [3,36]. Table 14 presents the characterization of biodiesel from studies in which the fuel was produced from oils with high free fatty acid content. It is possible to observe from the data a slight difference between the properties obtained by each study.

Table 14. Specifications of biodiesel from oils with high free fatty acid content.

Property	**Unit**	**Ullah** et al. [11]	**Reddy** et al. [99]	**Sabudak** et al. [100]	**Bouaid** et al. [101]
Feedstock		Waste palm oil	Jatropha oil	WCO	WCO
Initial Acid Value	$\frac{mg\ KOH}{g}$	4.03	17	4.60[a]	1.3
Density at 15 ℃	$\frac{Kg}{m^3}$	879	830	885	810
Acid Value	$\frac{mg\ KOH}{g}$	0.41	0.15[a]	0.38	0.06
Viscosity at 40 ℃	$\frac{mm^2}{s}$	5.24	4.27	4.92	4.96
Water content	$\frac{mg}{kg}$	0.03[a]	210	422	110
Flash point	℃	174	175	148	-

a: Value in %.

Figure 20 shows the GC-FID chromatogram obtained after the derivatization of sunflower oil, and Figure 21 shows the one for waste cooking oil.

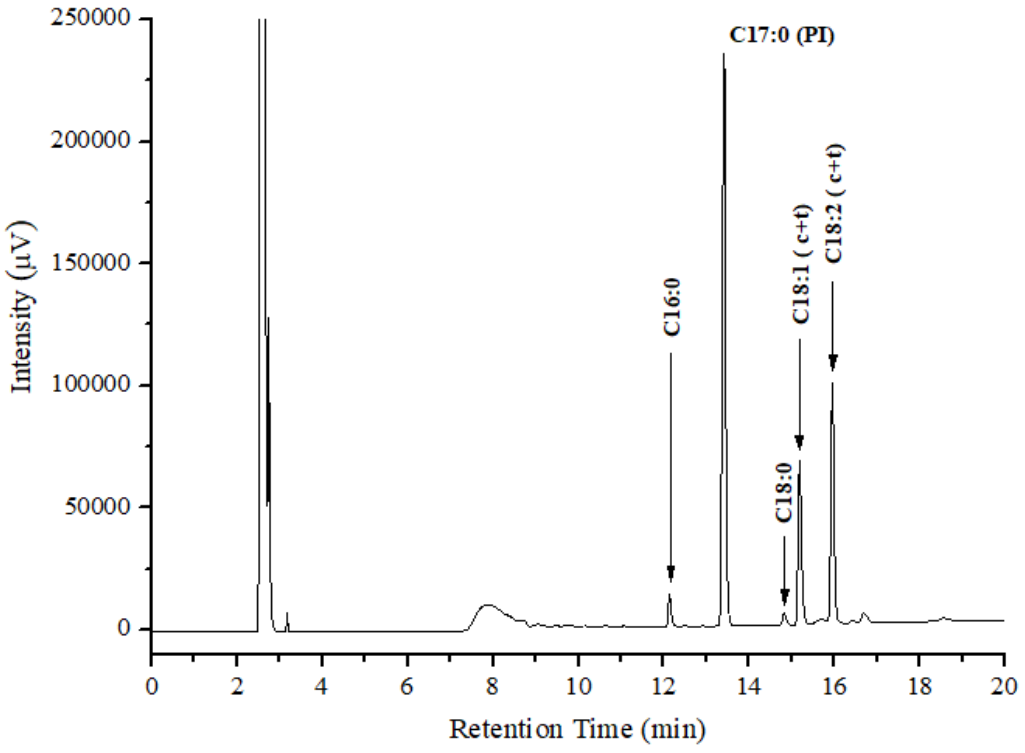

Figure 20. Chromatogram obtained after the derivatization of sunflower oil.

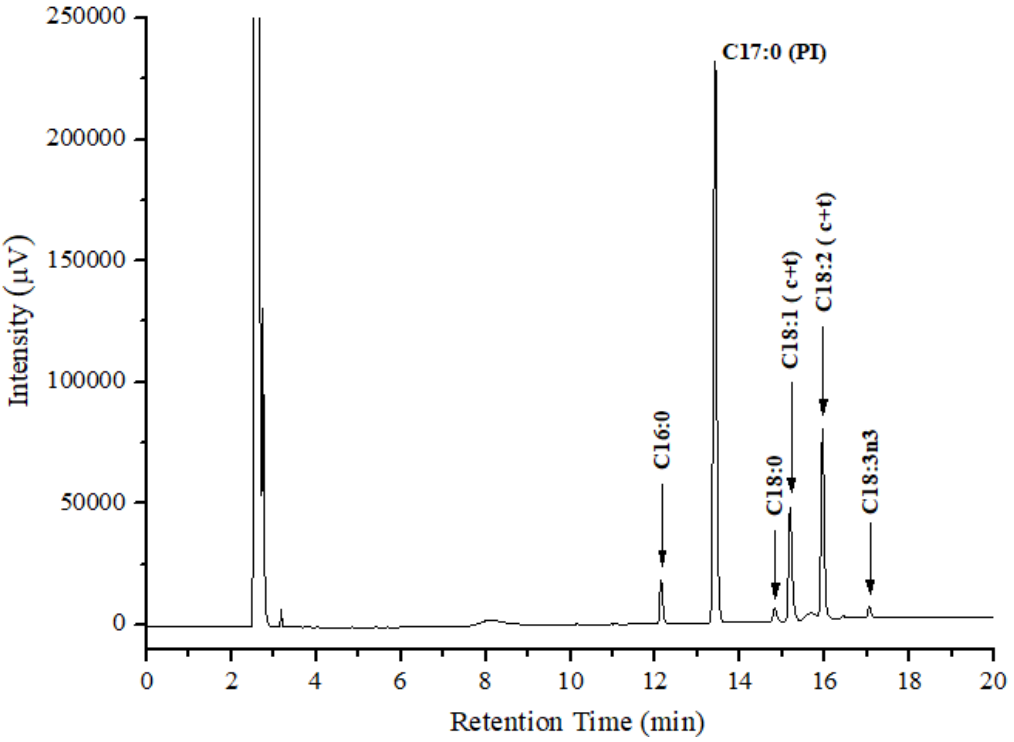

Figure 21. Chromatogram obtained after the derivatization of waste cooking oil.

These data were found to be in agreement as reported in the literature by Santana et al. (2016) [102], Jain et al. (2011) [81], Ambat et al. (2018) [7], and Babajide et al. (2010) [103], as can be seen in Table 15, which presents the FFA profile for sunflower oil and waste cooking oils reported by these authors.

Table 15. Fatty acid composition of SFO and WCO present in the literature.

Feedstock	**Composition of FFA (%)**								**Ref.**
	C16:0	**C16:1**	**C18:0**	**C18:1**	**C18:2**	**C18:3n3**	**C20:0**	**C20:2**	
SFO	12.44	-	4.51	23.3	55.03	4.74	-	-	[102]
SFO	10.4	0.35	4.7	24.8	52.5	6.5	0.75	-	[81]
WCO	8.5	-	3.1	21.2	55.2	5.9	-	-	[7]
WCO	4.1	2.4	1.4	40.5	38	10.6	0.8	1.6	[81]
WCO	14.0	-	6.02	35.6	44.78	0.6	-	-	[103]

The acid value (AV) for both samples of feedstock was determined in triplicate, and the results are presented in Table 16. The acidity value found for the waste oil was higher than that of virgin oil, as expected since WCO contains a higher quantity of FFA.

Table 16. Acid value data obtained for the raw materials.

Oil Sample	Mass (g)	V_{KOH} (mL)	C_{KOH} ($mol.L^{-1}$)	AV ($mg_{KOH}.g^{-1}$)	AV Average ($mg_{KOH}.g^{-1}$)
SFO	4.9970	0.18*	0.09374	0.1894	0.18
	5.0124	0.16*	0.09374	0.1679	
	5.0074	0.16*	0.09374	0.1681	
WCO	0.5006	0.615	0.09374	6.4612	6.14
	0.5035	0.582	0.09374	6.0793	
	0.5087	0.570	0.09374	5.8931	

*Measurements done with micropipettes of 20 µL

FT-IR spectroscopy was also used for SFO and WCO characterization. Figure 22 presents the FT-IR spectra of both oils. The strongest peak in the spectrum at 1743 cm^{-1} is assigned to the carbonyl group C=O since esters show a very strong band for the C=O group in the range of 1750-1735 cm^{-1} for normal aliphatic esters. The stretching vibration's bands with the stronger and broader one at 1160 cm^{-1} correspond to the C-O group. The peaks at 2923 cm^{-1} and 2853 cm^{-1} are assigned relative to the stretching vibrations of symmetric and asymmetric aliphatic C-H in the CH_2 and the terminal CH_3 groups. Also, the peaks in the region of 1200-1400 cm^{-1} are mostly assigned to the CH_2 and CH_3 aliphatic groups bending vibrations like symmetric H-C-H, bending at 1377 cm^{-1} and CH_2 scissoring at 1464 cm^{-1}. The band at 722 cm^{-1} is ascribed to the rocking vibration of all CH_2 groups in the ester chain, featuring the so-called long-chain band. The FT-IR spectrum of the waste cooking oil was found very similar to the sunflower oil due to the chemical nature similarities of the oils since the applied WCO was initially a sunflower oil [61,99].

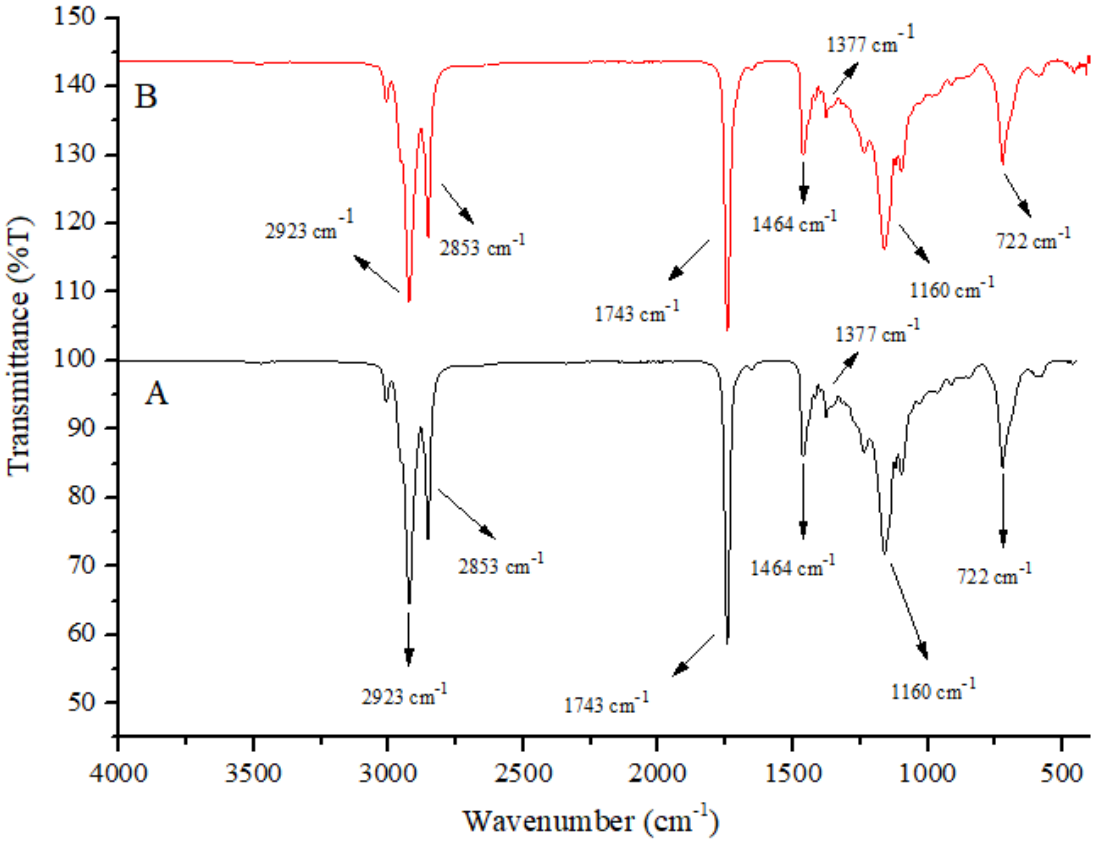

Figure 22. (A) FT-IR spectrum of sunflower oil. (B) FT-IR spectrum of WCO.

As in the industry, the treatment of used oil before transesterification is commonly applied due to its profitability, as mentioned in Section 2.4.1, it was considered for this study the performance of esterification to correct the high acid value of the WCO. In terms of time savings, the sunflower oil was used, which represents a great similarity to the WCO after treatment.

5.3 ChOH IONIC LIQUID

As stated in Section 5.1, it was chosen not to proceed using IMC_2OH IL, and to continue the research, choline hydroxide ionic liquid, also of a basic character, was selected. ChOH was purchased in a 45 wt.% methanol solution, so to confirm the concentration of the IL solution for the transesterification reactions, a titration was performed.

It was found out that the mass percentage of ChOH in the solution was 36.66%, and the titration data is shown in Table 17.

Table 17. 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	13.40	0.001201	0.1456	36.41	36.66
0.4078	13.52	0.001212	0.1469	36.73	
0.4041	13.50	0.001210	0.1467	36.68	
0.4030	13.55	0.001215	0.1473	36.81	

*[HCl]=0,08966 mol.L^{-1}

Figure 23 presents the FT-IR obtained for the ChOH ionic liquid solution in methanol, which structure was previously shown in Figure 11. The band of greatest interest for biodiesel catalysis is the one designated by the OH stretch associated with hydrogen bond at 3265 cm^{-1}. The characteristic absorptions of choline hydroxide are those represented by the C-N bond and the $(CH_3)_3N^+$ group of choline which are observed at 951 cm^{-1} and 1478 cm^{-1} respectively [104]. Besides, since this is a solution of choline hydroxide in methanol, the C-O stretching vibration appears in the spectrum at 1031 cm^{-1}. The peak at 2815 cm^{-1} is assigned relative to the stretching vibrations of symmetric and asymmetric aliphatic C-H in the CH_2 and the terminal CH_3 groups.

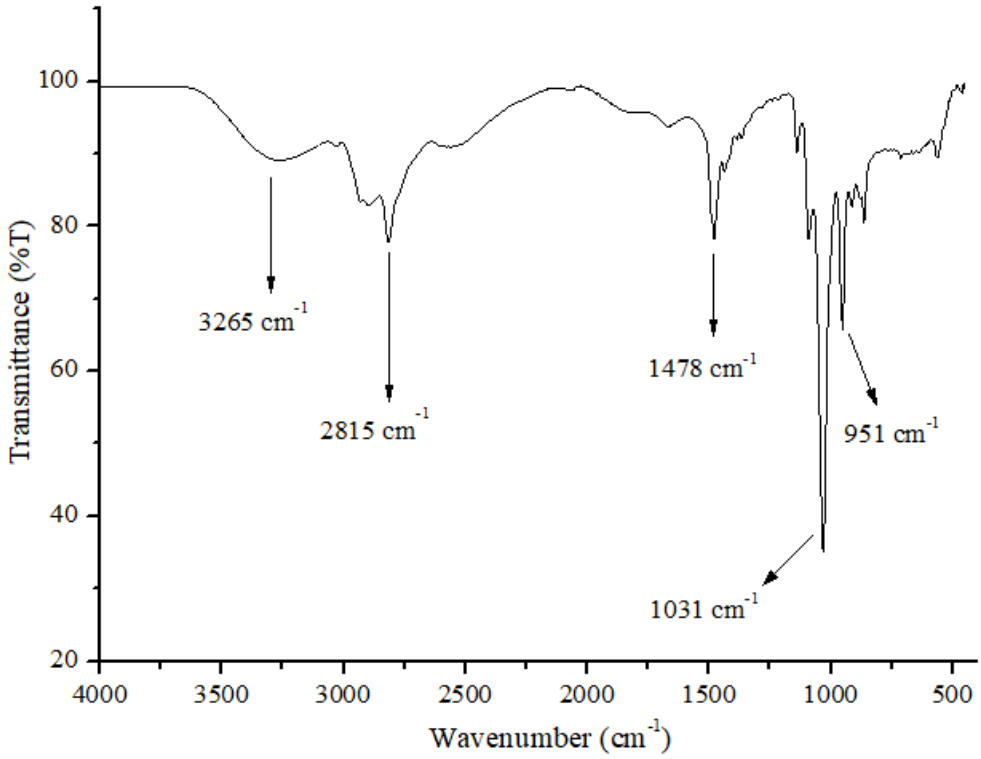

Figure 23. FT-IR spectrum of choline hydroxide solution, 45 wt.% in methanol.

5.4 KINETIC STUDY

First, two reactions were performed to determine the catalyst load parameter that would be used for the kinetic study in order to obtain the best conversion rate of methyl esters. Thus, catalyst concentrations of 1 and 2 wt.% in relation to the oil were evaluated. Based on the works published in the literature on transesterification with ChOH [64,75,76,99], the reactions in this study were carried out at 65 °C, for 4h using a molar ratio of oil/methanol of 1:10.

The data on the quantities of reagent used, as well as the conversions obtained by mass and amount of methyl esters, are shown in Table 18. Also, in Figure 24 A is represented the separation of the phases, in which the upper phase was FAMEs presenting a lighter color. The lower phase was the mixture of IL, glycerol, and methanol, and in Figure 24, B is demonstrated the aspect of the phases after the process of separation and drying.

Table 18. Data of the preliminary tests for transesterification parameters determination.

	Reaction Parameters				**Reagents Weighting**			**Conversion Values**	
Test	**Time (h)**	**Temp. (°C)**	**Oil/MeOH (mol)**	**%ChOH**	**ChOH Mass (g)**	**Oil Mass (g)**	**V MeOH (mL)**	**Mass (%)**	**%FAMEs**
T1	4	65	1:10	1	0.2081	20.0261	9.24	92.46	83.52
T2	4	65	1:10	2	0.4041	20.0028	9.18	91.89	88.97

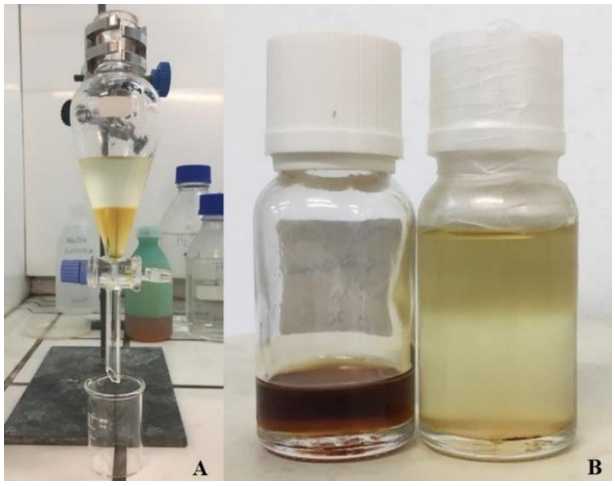

Figure 24. A: Representation of the phase separation obtained after the reaction: the upper phase is FAMEs, and the lower phase is the mixture of unreacted methanol, glycerol, and catalyst. B: Visual appearance of the separated phases after drying. Left flask: lower phase. Right flask: upper phase.

By the comparison of the ChOH catalytic activity in the transesterification reaction, a higher yield in esters was achieved with 2% concentration of catalyst, as shown in Table 17. Therefore, it was selected for the following experiments.

From the determination of the following reaction parameters: 65 ℃, catalyst dosage of 2%, and 1:10 oil/MeOH molar ratio, the transesterification reactions were performed with sunflower oil and methanol for the periods of 10, 20, 30, 45, 60, 120, 240, 360, and 480 minutes. The results obtained for percentage in FAMEs calculated according to Expression 2 presented in Section 4.4.1 for each time analysis are shown in Table 19.

Table 19. Kinetic study data for temperature 65 ℃.

Test	Time (min)	Oil Mass (g)	ChOH Mass (g)	Methanol (mL)	Organic Phase (g)	Catalyst Phase (g)	%FAMEs
C1	10	20.0058	0.4025	9.18	20.4482	3.5826	68.71
C2	20	20.0110	0.4019	9.18	18.5963	2.7722	86.01
C3	30	20.0209	0.3993	9.17	16.9321	3.8084	84.92
C4	45	20.0401	0.4085	9.19	17.2505	3.4610	86.50
C5	60	20.0084	0.4035	9.18	18.5910	2.7045	84.88
C6	120	20.0270	0.4032	9.18	17.3737	3.6083	82.94
C7	240	20.0188	0.4115	9.20	16.8003	4.1015	88.97
C8	360	20.0092	0.4026	9.18	17.2238	3.3607	88.28
C9	480	20.0115	0.4012	9.17	17.4928	3.5786	83.94

The values obtained for duplicate analysis of the samples until 60 minutes are shown in Table 20, and the kinetic reaction curve for choline hydroxide is presented in Figure 25.

Table 20. Results of FAME conversion analysis in duplicate for the samples until 60 minutes.

Test	Time (min)	%FAMEs		
		1	2	Average
C1	10	68.71	67.46	68.09
C2	20	86.01	82.85	84.43
C3	30	84.92	85.50	85.21
C4	45	86.50	83.76	85.13
C5	60	84.88	84.66	84.77

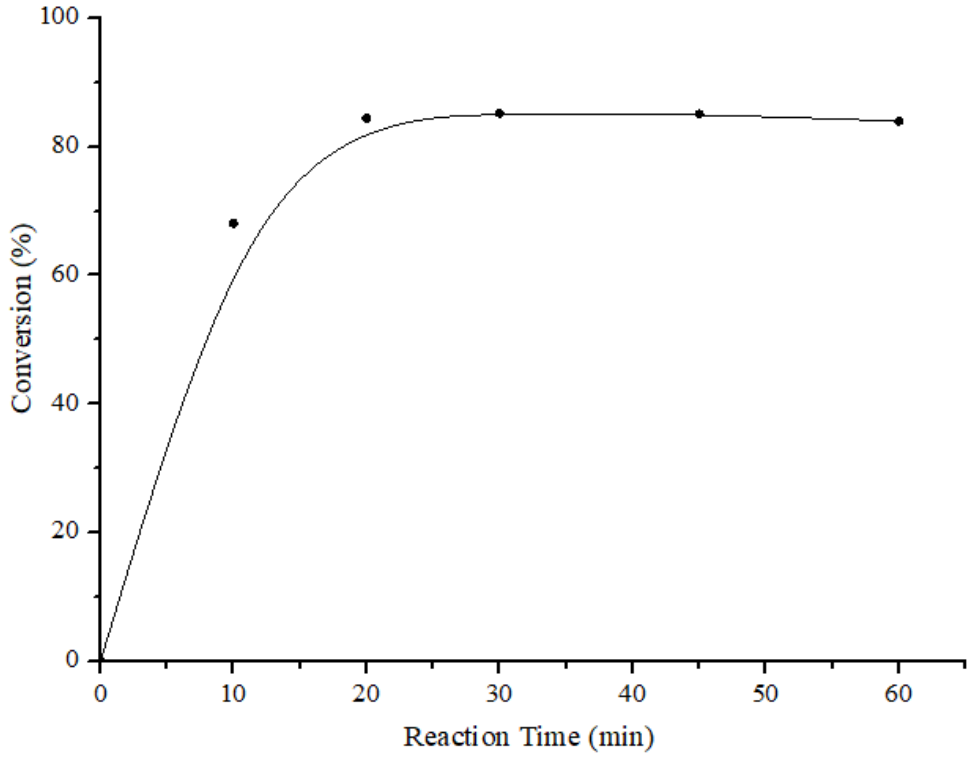

Figure 25. Kinetic curve for ChOH. Parameters: T= 65ºC, oil:alcohol = 1:10, % catalyst = 2 (w/w).

From the kinetic curve, it can be seen that the time necessary for the equilibrium to occur is close to 20-30 min, obtaining a conversion rate of methyl esters of approximately 84.80%.

As indicated in Section 2.4.2.2, 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.

$$TAG + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} DAG + R'CO_2R \quad (3)$$

$$DAG + ROH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} MAG + R'CO_2R \quad (4)$$

$$MAG + ROH \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} GL + R'CO_2R \quad (5)$$

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) [77,81,102], 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.

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

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

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.

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

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

$$-ln(1 - X) = kt \tag{10}$$

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

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

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

Table 21 summarizes the data obtained for each proposed reaction order.

Table 21. Data for each reaction order proposed at 65 °C.

Time (min)	**Conversion (%)**	**0th Order** X	**1st Order** $-\ln(1-X)$	**2nd Order** $\frac{X}{1-X}$	**3rd Order** $\frac{1}{2(1-X)^2}$
0	0.0000	0.0000	0.0000	0.0000	0.5000
10	0.6808	0.6808	1.1419	2.1328	4.9073
20	0.8443	0.8443	1.8579	5.4103	20.5457
30	0.8521	0.8521	1.9105	5.7568	22.8269

In this approach, the rate constant *k* is obtained by plotting a graph of the function 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 [105].

Although 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 [77,81,102], after performing the data fit in Origin Software, the best result was found for order 2, as presented in Table 22.

Table 22. Coefficient of determination obtained by applying the integral method for each reaction order.

Order	**Statistics Adj. R^2**	**Angular Coefficient**	**Angular Coefficient Error**
0	0.88129	0.03518	0.00635
1	0.93713	0.07564	0.00971
2	0.96590	0.21588	0.02019
3	0.95671	0.81771	0.08649

As can be seen in the Table above, the coefficient of determination (R^2) showed low values. This result may be due to the fact that only a few experimental data could be useful to plot a line that would satisfactorily fit them, since, for the analysis of the reaction kinetics, only the points prior to the equilibrium state should be considered. Also, the chosen kinetic model assumes only the direct reaction and does not take the kinetics of the reverse reaction into account.

From this test at 65 °C, it was concluded that the transesterification reaction with ChOH occurred quickly, which was not expected because in the literature the optimal reaction times found for choline hydroxide were 2.5 to 4 hours when applied catalyst concentrations of 4-10% and oil /MeOH molar ratio around 1:10, as presented in Section 3.3.2 about choline hydroxide. When applying larger amounts of catalyst and temperatures close to 65 °C, Fan et al. (2013) [64] reported that ChOH showed the best catalytic performance at 2.5 hours, Anjos (2018) [76] concluded on an optimal reaction time around 3 hours, and Reddy et al. (2014) [99] reported a reaction time of 4 hours.

As a result, it would be interesting to investigate the reaction behavior for times lower than 30 minutes. Figures 26 and 27 represent the graph plotted by the linear adjustment for orders 2 and 3, respectively, with only the data from the first reaction times.

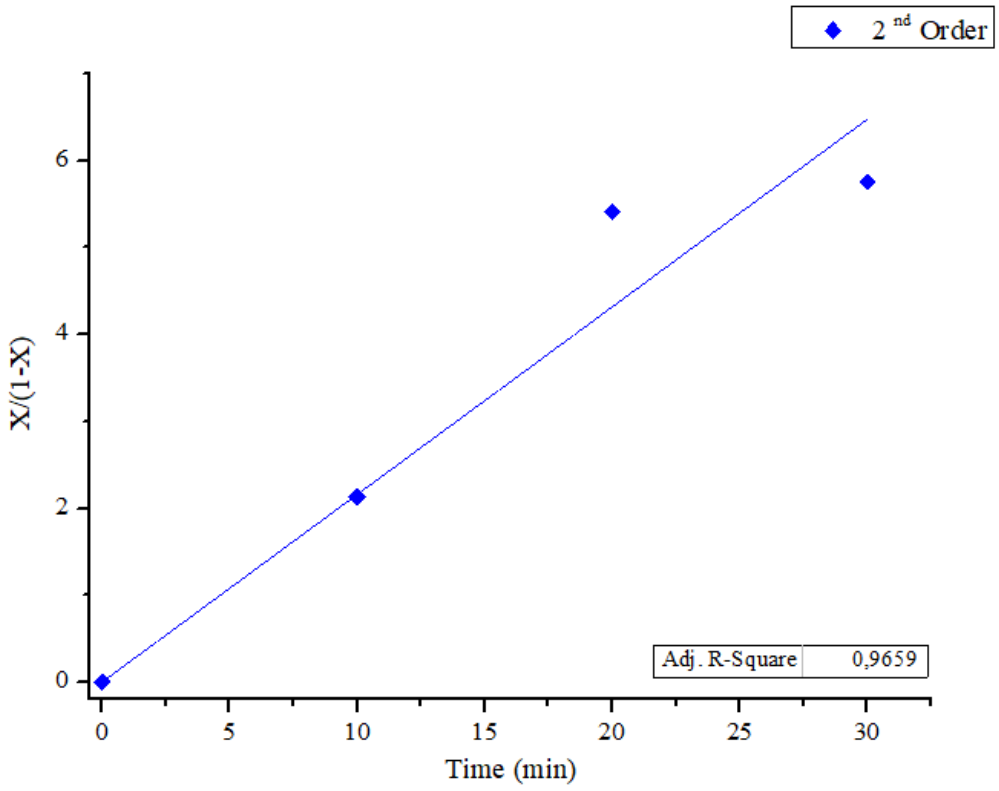

Figure 26. Plot of $\frac{X}{1-X}$ vs time (min).

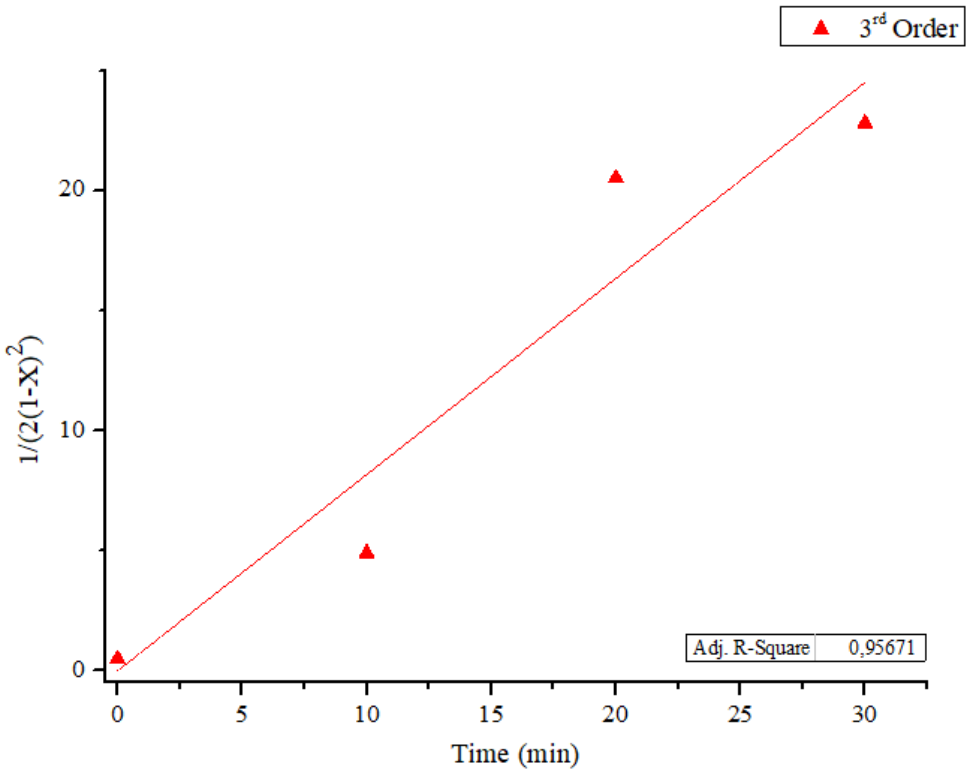

Figure 27. Plot of $\frac{1}{2(1-X)^2}$ vs time (min).

Based on this result, the value estimated for the reaction constant *k* for the second-order model was 0.2930 $L.mol^{-1}.min^{-1}$.

A similar result was reported by Foon et al. (2004) [82] for the transesterification reaction of palm oil with methanol using sodium hydroxide. It was found that the data could be reasonably described by a second-order rate expression, and a rate constant of 0.163 $L.mol^{-1}.min^{-1}$ was found by applying a catalyst concentration of 0.1250 $mol.kg^{-1}$ oil, an oil/MeOH molar ratio of 1:10 at 60 °C.

Another study that reported a second-order reaction was done by Kumar et al. (2011) [83] in which jatropha oil was transesterified using methanol and 1 wt.% KOH as the catalyst. Kinetics, modelled as a single-step reaction, revealed that the order of the reaction was 2 with respect to the triacylglycerol concentration and 1 in relation to the methanol concentration, with a rate constant of 1.26 $L^2.mol^{-2}.min^{-1}$.

With regard to other studies found in the literature, due to different kinetic model from the one used in this work, a better comparison could be made concerning the activation energy value. However, unfortunately, it was not possible to carry out the experiments for the previously desired temperatures of 35 and 45 °C.

Pascoal et al. (2020) [106] investigated the kinetics of ultrasonic transesterification from almonds with basic catalyst KOH (5 wt.%), and although it was

concluded that experimental kinetics of the transesterification reaction was better fit to the first-order kinetic model, the rate constants were calculated to each temperature considered for a second-order model. When a temperature of 40 °C was applied for the reaction, it was found a rate constant of 0.401 $L.mol^{-1}.min^{-1}$. For the first-order model, a rate constant of 0.0138 min^{-1} was determined, and the activation energy of the ultrasound-mediated in situ transesterification reaction was estimated at 27.53 $kJ.mol^{-1}$. The transesterification rates in this study are higher than those observed in the present work, but it must be pointed out the use of ultrasound technology and a higher quantity of catalyst.

To summarize, the considerably short reaction time is the most distinct aspect of the results in this study compared to previous studies conducted on ionic liquids in mechanical stirrers.

5.5 ChOH IONIC LIQUID RECOVERY

5.5.1 Butanol/Water Solvent Extraction

The first tests were carried out according to what was exposed by Fan et al. (2013) [64], who stated that choline hydroxide could be removed from glycerol from biodiesel production by a liquid extraction using a mixture of water and 1-butanol as the extracting agent, in which glycerin is distributed in greater quantities in the water phase and choline hydroxide in the butanol phase.

For this procedure, 1 gram of the catalyst phase was used, the volume ratio of butanol/water was fixed 1:2, and the mass ratio of the catalyst phase in relation to the total weight of the solvents was varied in the proportions of 1:1, 1:2 and 1:3. It was observed that there was no phase separation as desired, even though the amount of butanol added was much higher than the amount considered miscible in water [107].

In Figure 28 is represented the test of 1:2 butanol/water, in volume, and 1:2, in mass, of the catalyst phase to the total weight of the solvents, in which no phase separation was observed.

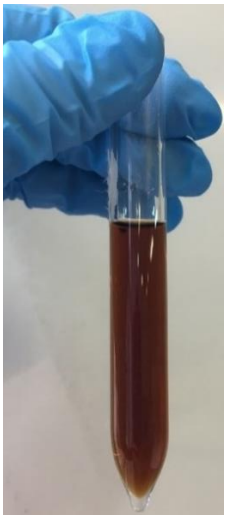

Figure 28. Test 1:2 (v/v) BuOH/water, 1:2 (w/w) catalyst phase/solvent mixture.

From this result, two preliminary tests were carried out, one with another proportion in volume of butanol and water, and another with diethyl ether and water. Diethyl ether was selected for this attempt because it is less dense than water and, also poorly soluble in it. Both tests were performed by adding 4 mL of water and 4 mL of butanol or diethyl ether to 1 g of catalyst phase. Thus these tests were performed with a volume ratio of solvents of 1:1, and a mass ratio of catalyst phase to the total weight of the solvents of 1:7. It was decided to add an excess amount of solvents to assess their influence on phase separation. Phase separation was observed only in the test with butanol and water, so the study of the separation of choline hydroxide from glycerol was continued with butanol and water. Figure 29 A shows the result of the test with diethyl ether and water, and Figure 29 B the result with butanol and water.

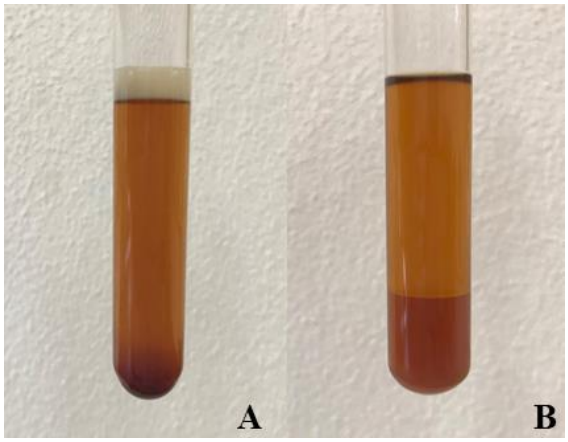

Figure 29. Preliminary separation tests. A: diethyl ether and water; B: butanol and water.

In sequence, separation tests with butanol were carried out with a 1:1 volume ratio and mass ratio from 1:1 to 1:6, being named as B1 to B6.

Table 23 presents the information of the solvents added in each test, the mass of the catalyst phase, the mass of the phases obtained after separation (P1 upper phase and P2 lower phase), as well as the masses after evaporation and drying of the phases, which P1.2 is the phase that was supposed to contain the IL, and P2.2 the phase that was supposed to contain only glycerol.

Table 23. Data for butanol/water tests.

Test	Specification		Initial Weighing			Phases Weighing		Final Weighing		
	Butanol: Water (v/v)	**Cat. Phase: Solvents (w/w)**	**Catalyst phase (g)**	**Water (g)**	**BuOH (g)**	**P1 (g)**	**P2 (g)**	**P1.1 (g)**	**P1.2 (g)**	**P2.2 (g)**
B1	1:1	1:1	1.0017	0.5628	0.4694	-	-	-	-	-
B2	1:1	1:2	1.0207	1.1280	0.9256	-	-	-	-	-
B3	1:1	1:3	1.0125	1.6716	1.3511	-	-	-	-	-
B4	1:1	1:4	1.0093	2.2191	1.8156	4.4876	0.3004	1.0040	1.8728	0.0321
B5	1:1	1:5	1.0206	2.7786	2.2854	5.0051	0.6973	0.9637	1.8906	0.0672
B6	1:1	1:6	1.0293	3.3212	2.7208	5.4332	1.3314	0.6235	1.7288	0.1070

Tests B1, B2, and B3, remained as homogeneous mixtures, whereas in tests B4, B5 and B6, two phases were formed with a well-defined interface. The phase separation occurred only in some systems because the 4-component system created for the proportions shown in B4, B5, and B6 tests was not stable, so they were divided into two liquid phases with different compositions to achieve liquid-liquid equilibrium [108]. Figure 30 shows the phase separation obtained in these tests.

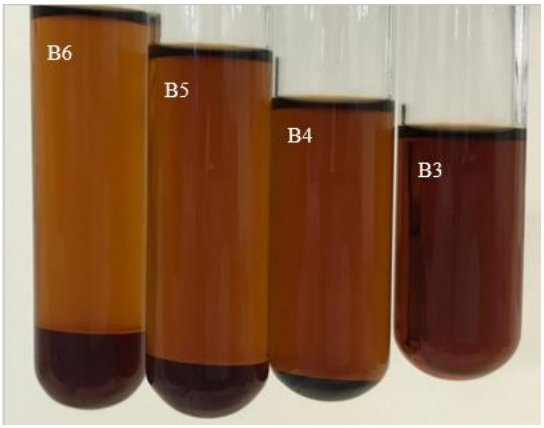

Figure 30. Phase separation tests B3, B4, B5, and B6.

The composition of each of the phases obtained was investigated by FT-IR spectroscopy.

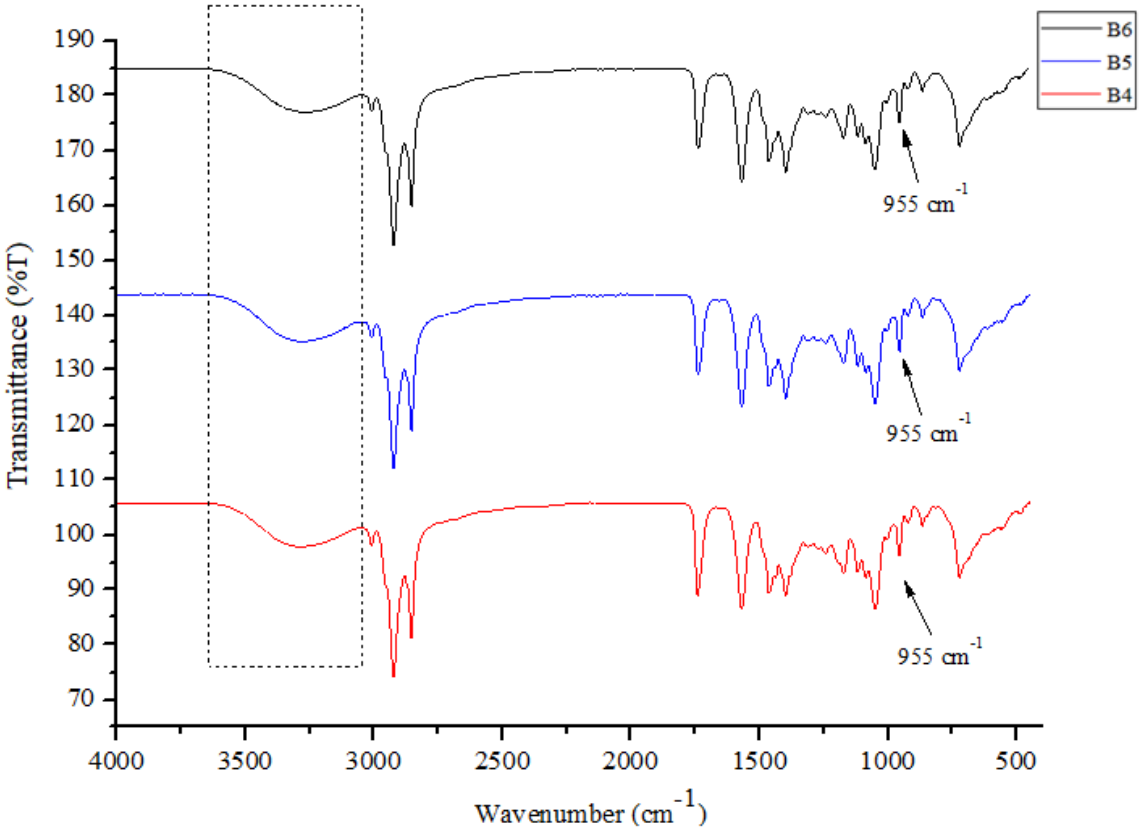

Figure 31. FT-IR spectra of phases P1.1.

From the FT-IR images of phases P1.1 of tests B4, B5, and B6 shown in Figure 31, it is possible to observe a band at 955 cm^{-1}, which may be due to C-N stretching characteristic of the ionic liquid. Besides that, it can be seen that the broad peaks of hydrogen bonds around 3275 cm^{-1}, highlighted by the dotted rectangle, present lower values of transmittance in relation to those seen in P2.2 phases of glycerol (see Figure

32), which show a similar appearance to the ChOH O-H band than the one seen in the glycerol spectrum.

For comparison, the FT-IR spectrum of a glycerol sample is shown in Figure 33. The broad peak at 3292 cm^{-1} is assigned to O-H stretching vibrations. The peaks at 2933 cm^{-1} and 2878 cm^{-1} are attributed to the elongation of aliphatic C-H bonds. The strong band of the spectrum at 1030 cm^{-1} is ascribed to stretching vibration C-O, which occurs in the range of 1260-1000 cm^{-1} for alcohols, and the weak peak at 1413 cm^{-1} is assigned to C-O-H. The band at 922 cm^{-1} can be attributed to C-O stretching, of CH_2-OH, which occurs between 900 and 800 cm^{-1} [96].

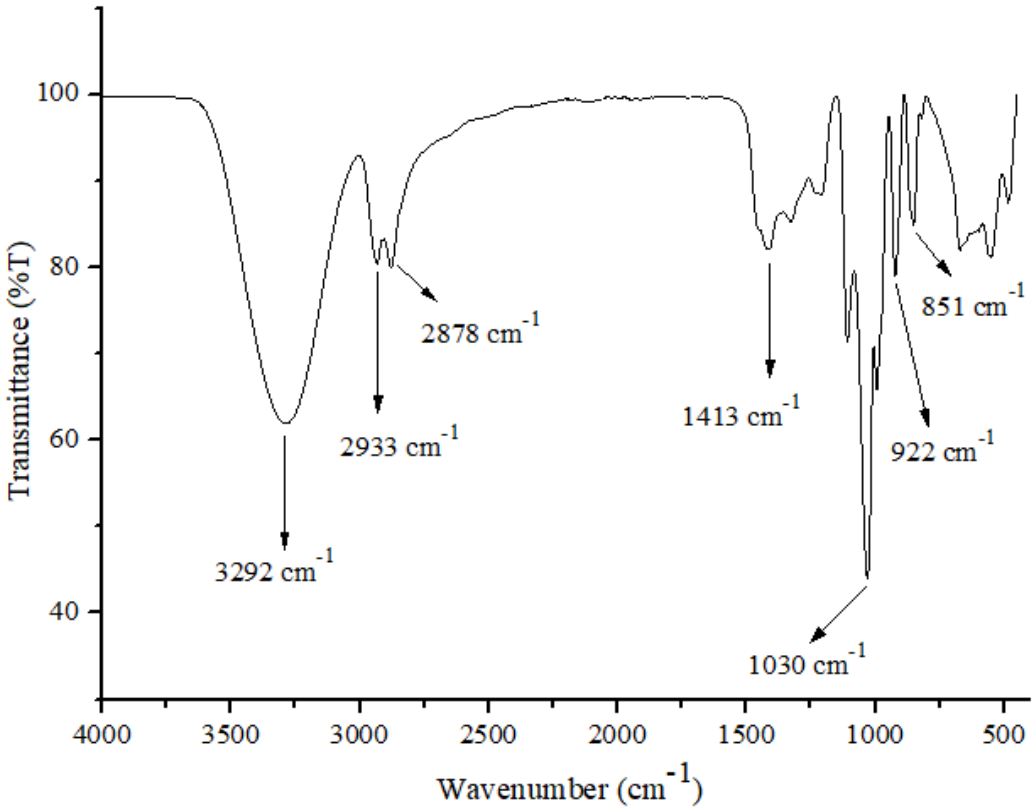

Figure 32. FT-IR spectrum of glycerol.

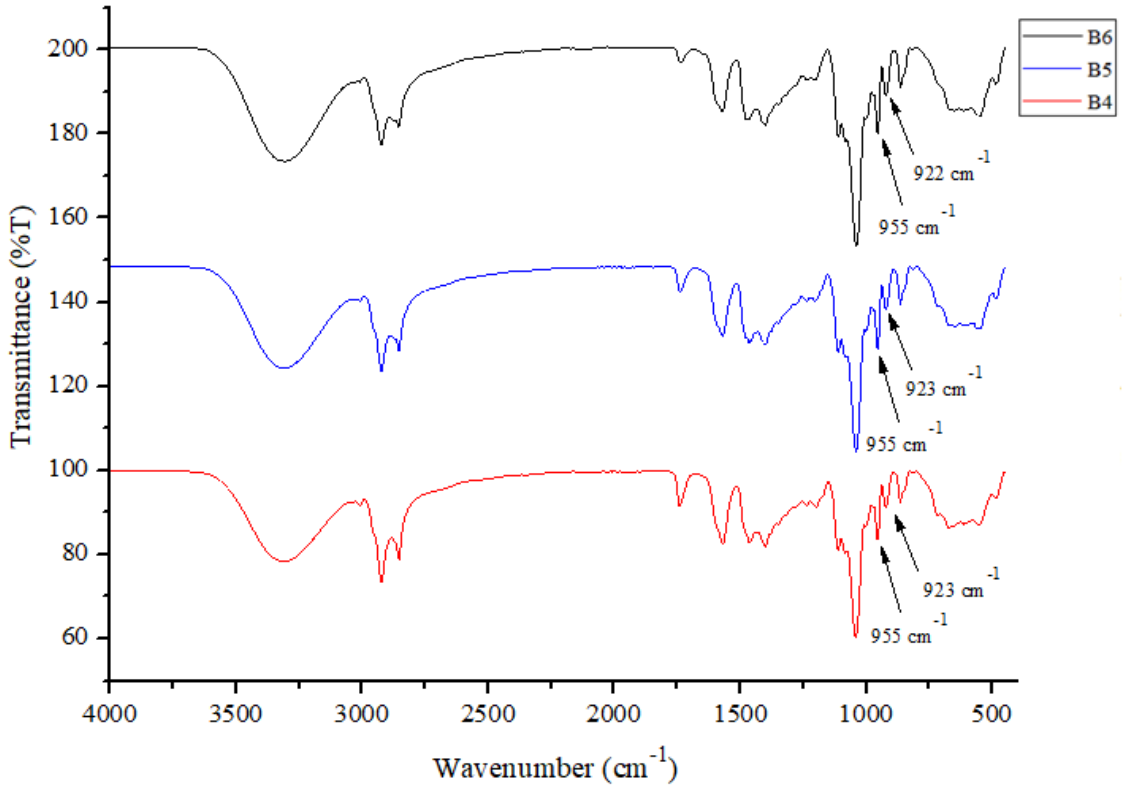

Figure 33. FT-IR spectra of phases P2.2.

As can be seen in Figure 33, which shows the spectra of the three analysis for phase P2.2, although this phase exhibit characteristic glycerol peaks such as a strong band for O-H and C-O vibration (at 3300 cm^{-1} and 1040 cm^{-1}), as well as the bands at 922 cm^{-1}, which is present only in the glycerol spectrum, a band is visualized at 955 cm^{-1} as outlined in the figure. Therefore, it is possible to conclude that although there was some separation of ionic liquid from glycerol, a quantity of ChOH still remained in the glycerol phase.

Besides that, as shown in Table 23, a significant amount of water remained in the upper phase (P1), which was not expected, so that P2.2 phase, which should contain the largest amount of glycerol, showed a low value.

A similar result was obtained by Bessa (2015) [75], who carried out the study of the choline hydroxide partition in the quaternary system water+glycerin+choline hydroxide+1-butanol at 30 °C, concluding that choline hydroxide was present in greater quantity in the water-rich phase with the presence of glycerin in the system (P2.2).

5.5.2 Ethyl Acetate/Water Solvent Extraction

Anjos (2018) [76] cited the possibility of washing the catalyst phase with ethyl acetate to remove the methyl esters from this phase. In this study, an attempt was made

to separate choline hydroxide from glycerol, from a liquid-liquid extraction with water and ethyl acetate, due to the low solubility of ethyl acetate in water and its low toxicity [109].

Table 24 presents the data regarding the separation tests. P1 is the upper phase and P2 the lower phase obtained after phase formation, P1.1, and P2.1 correspond to these phases after drying, respectively.

Table 24. Data for ethyl acetate separation tests.

Test	Specification		Initial Weighing			Phases Weighing		Final Weighing	
	EtOAc: Water (v/v)	Cat. Phase: Solvents (w/w)	Catalyst phase (g)	Water (g)	EtOAc (g)	P1 (g)	P2 (g)	P1.1 (g)	P2.1 (g)
E1	1:1	1.1	0.5063	0.2637	0.2416	-	-	-	-
E2	1:1	1:2	0.5063	0.526	0.4821	-	-	-	-
E3	1:1	1:4	0.5029	1.0603	0.9676	0.6888	1.7258	0.055	0.4089
E4	1:2	1:2	1.0068	1.3863	0.621	2.4113	0.3928	1.2327	0.7612

Figure 34 shows the aspect obtained with the separation of phases of tests E3 and E4.

Figure 34. Test E3 1:1 (v/v) EtOAc/water, 1:4 (w/w) catalyst phase/solvent mixture.

It is possible to notice that the coloring of phase P1 is light, and the phase P2 shows a dark yellow color. This feature was not expected since choline hydroxide exhibits a dark brown-yellow color.

Figure 35 shows the FTIR spectrum of the catalyst phase used for test E3 compared to the spectrum obtained for the lower phase (P2). From the image, it is

concluded that there was no separation of glycerol from the ionic liquid since the obtained phase and the initial catalyst phase are equal. Also, Figure 36 shows that the P1 phase is not similar to ChOH. The black dotted rectangle highlights the 951 cm^{-1} band of the ionic liquid. It is possible to observe that it is not present in the P1 phase.

Besides that, the green rectangle shows the band at 1737 cm^{-1}, which characterizes the presence of C=O absorptions and at 1171 cm^{-1} of C-O stretching vibration, which may mean that the liquid-liquid extraction has only removed a trace of methyl esters from the catalyst phase since the phases were dried and the ethyl acetate was evaporated from the sample.

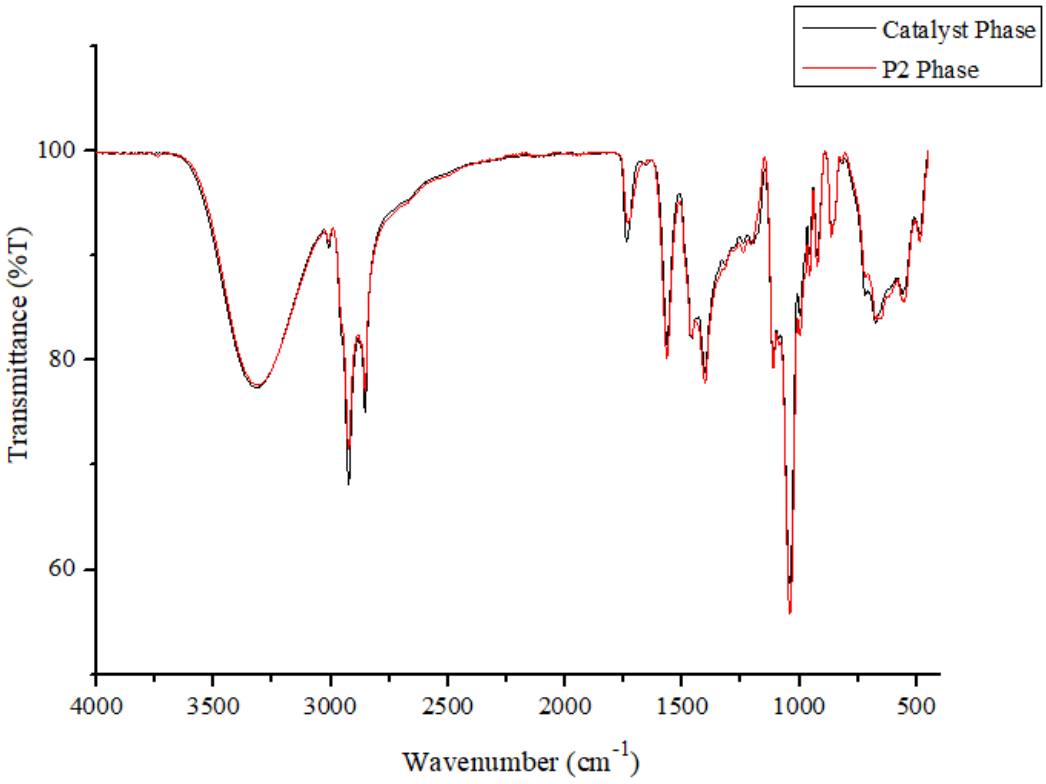

Figure 35. FT-IR spectra of the catalyst phase and P2 phase of test E3.

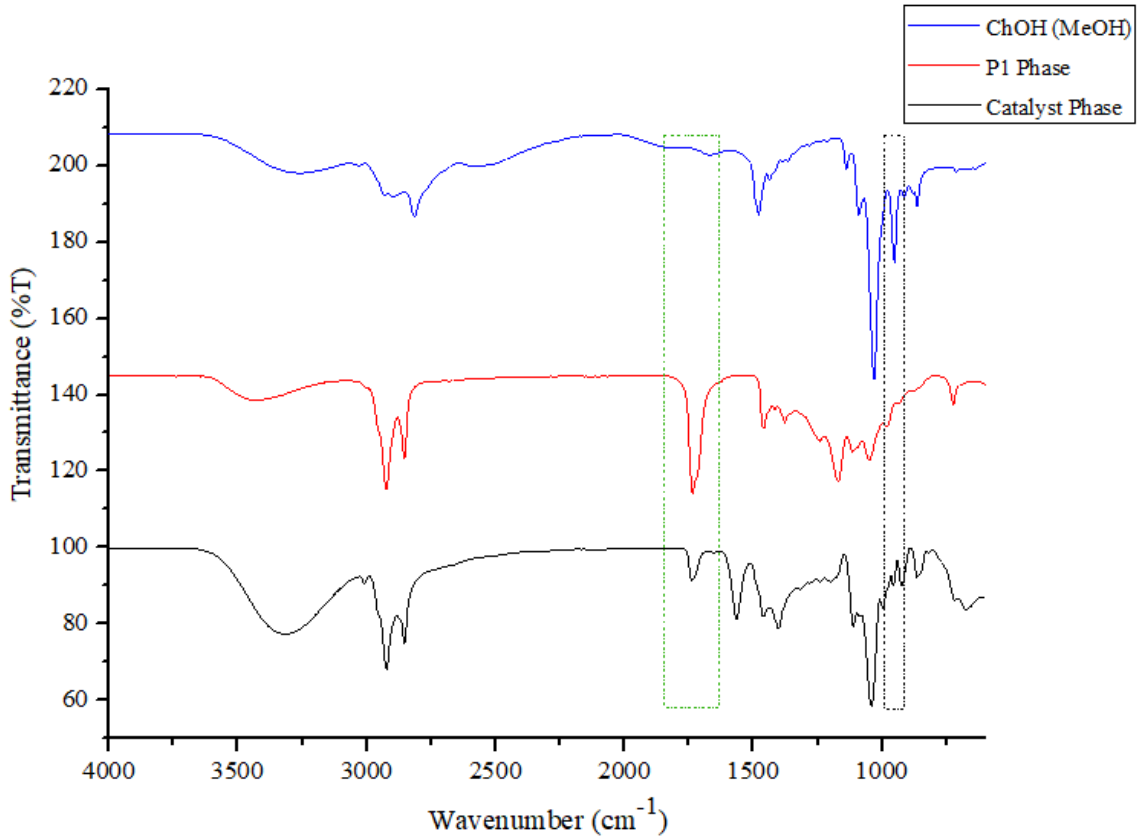

Figure 36. FT-IR spectrum of P1 phase compared to IL and catalyst phase spectra.

The results obtained for the E4 test were not satisfactory since the spectrum of the P1 phase was practically the same as that of the P2 phase. The comparison of FT-IR spectra of P1 and P2 phase is shown in APPENDIX A, Figure A.4.

6. CONCLUSIONS

The synthesis of the ionic liquid bis-(3-methyl-1-imidazole)-ethylene dihydroxide, proposed at the beginning of this study was not successful as previously stated in the literature since a reasonable conversion was not achieved for later industrial application. Thereby the determination of operational parameters such as reaction time, reaction temperature, alcohol/oil molar ratio and catalyst dosage for the production of biodiesel from waste cooking oil with this catalyst was not possible.

Besides, choline hydroxide proved to be an efficient catalyst for the triacylglycerol catalysis for the production of biodiesel, considering that a conversion of 85.21% in FAME content was obtained in only 30 minutes of reaction.

The results from the kinetic study carried out at 65 °C, with a molar ratio of oil/methanol of 1:10, and 2 wt.% of catalyst load indicated that second order was the best fit for the reaction, and its rate constant (k) was estimated as 0.2930 $L.mol^{-1}.min^{-1}$.

From the ionic liquid recovery, it was concluded that although there was some separation of the ionic liquid from the glycerol by the extraction with butanol and water, an amount of ChOH remained in the glycerol phase. For the attempt of extraction with water and ethyl acetate, it was concluded that the removal of ionic liquid from glycerol did not occur. However, the extraction was efficient in removing traces of esters from the catalyst phase.

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 waste oils with high FFA contents since ChOH revealed an excellent capacity for fast transesterification. Thus, based on a more detailed study of the optimal reaction parameters for ChOH and subsequent application of the recovered amount of this ionic liquid in new reaction cycles, there is a strong indication that its reuse as a catalyst will present good values for esters yield, which enables its possible industrial application.

6.1 SUGGESTIONS FOR FUTURE WORKS

In order to achieve a better conclusion on the applicability of IMC_2OH and ChOH ionic liquid in the production of biodiesel, it will be necessary to carry out further studies using the mentioned ionic liquids. Some suggestions for future work are:

(i) Study and application of a better solvent for the second synthesis step for the imidazolium-based ionic liquid IMC_2OH;

(ii) Perform kinetic studies for ChOH in short times between 0-30 minutes and at temperatures other than 65 ℃ such as 35 to 60 ℃.

(iii) Study of the application of the alkaline ionic liquids as catalysts for the transesterification of acidic waste cooking oils, pre-treated by esterification catalysed by acidic ionic liquids.

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

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

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APPENDIX A – ChOH Separation from Glycerol

Figure A.1 Catalyst used in the transesterification that produced the catalyst phase used for tests B4, B5, and B6.

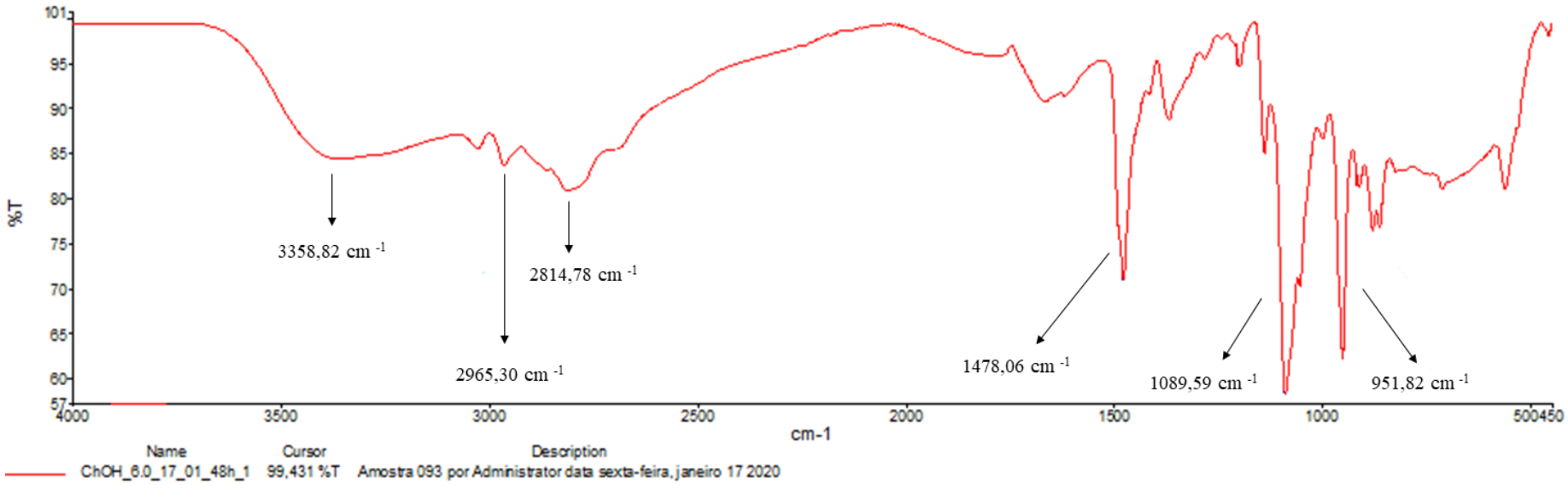


Figure A.2 Catalyst phase used for tests B4, B5, and B6.

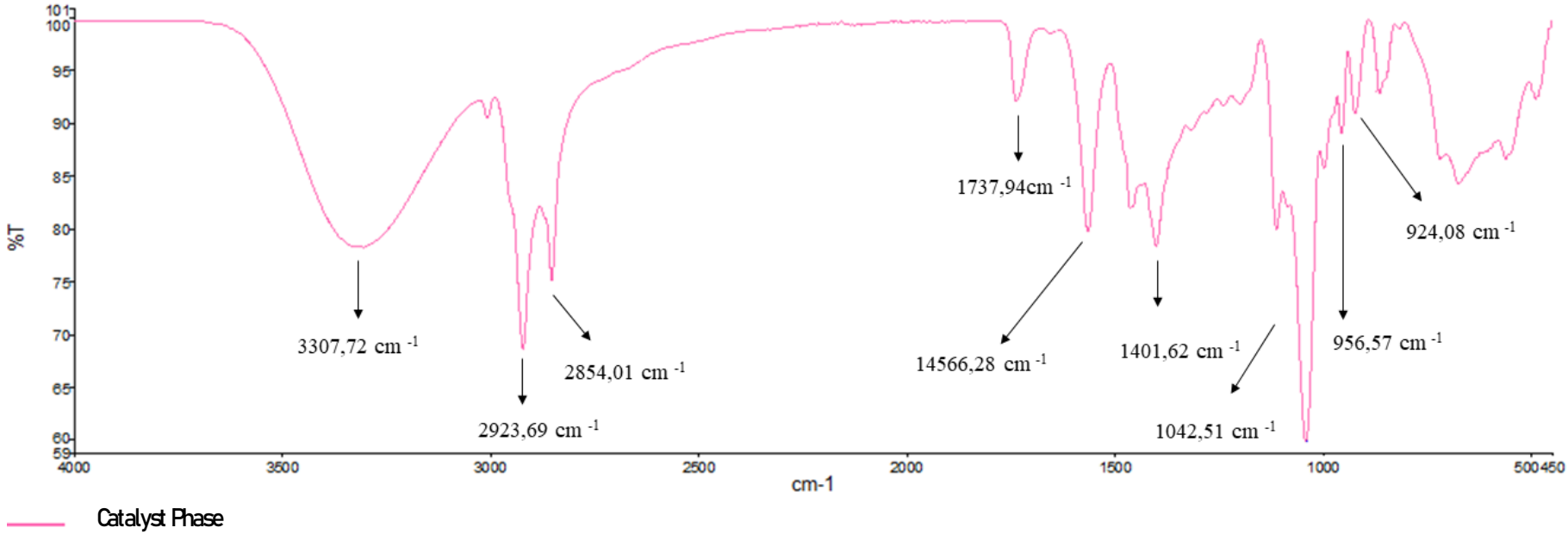


Figure A.3 Comparison of the P2.2 phase of B6 test with the catalyst used

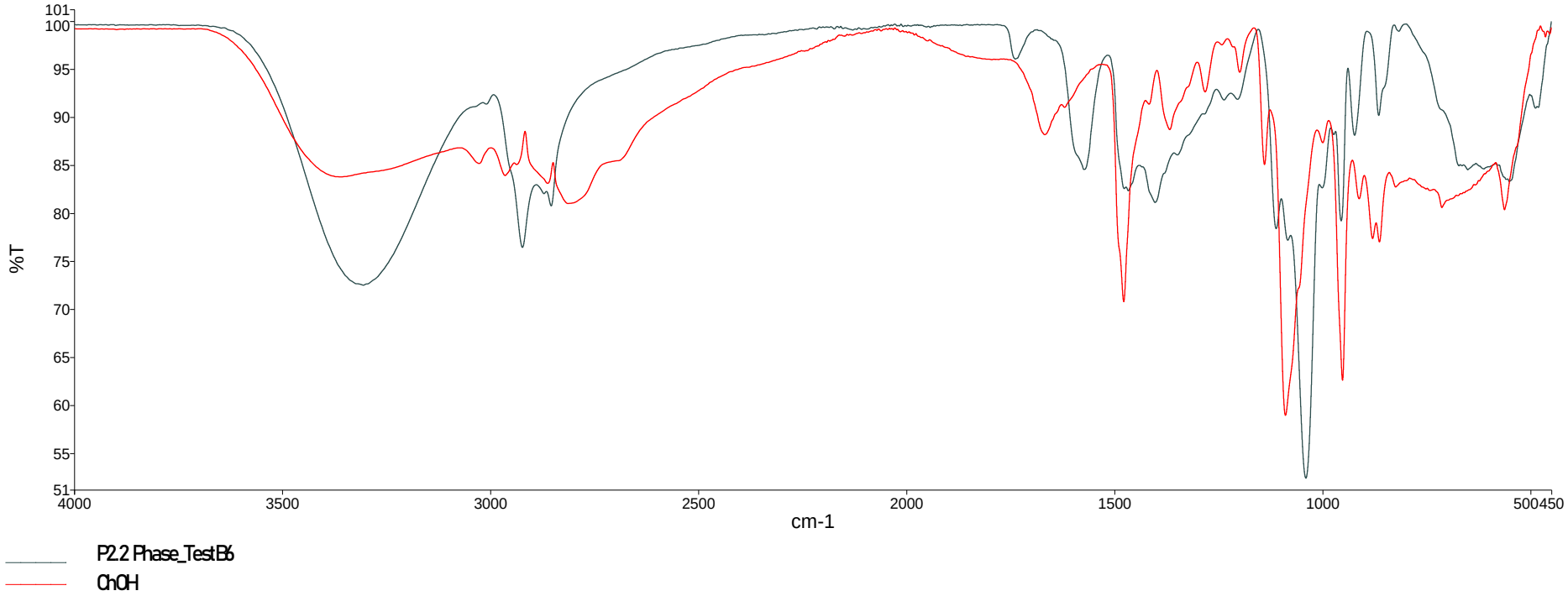
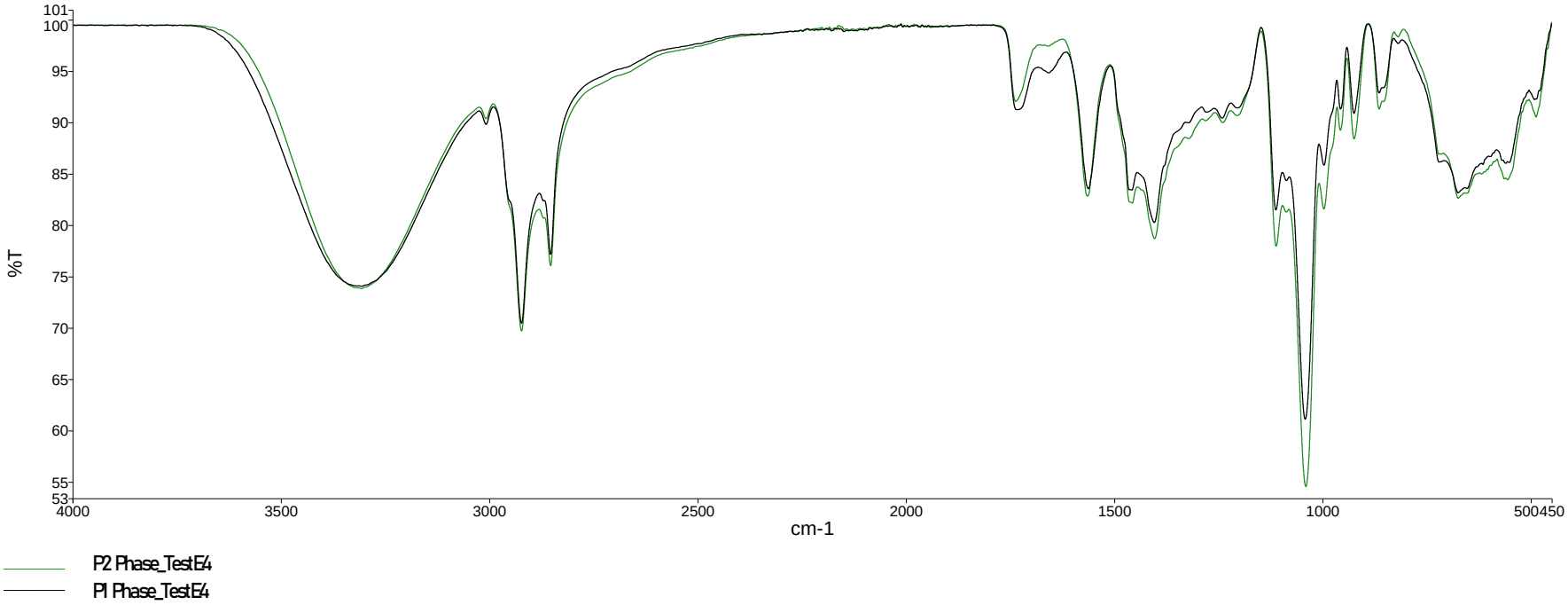


Figure A.4 Comparison of P1 and P2 phase spectra of test E4.



APPENDIX B – Conferences

B.1 – XXV Encontro Luso Galego de Química, Santiago de Compostela, November 2019.

CAT07

Study of the Performance of Alkaline Ionic Liquids for the Catalysis of Biodiesel Production from Waste Cooking Oil

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Fossil fuels are a primary energy resource that play a critical role in our daily activities. Currently, the provision of energy relies primarily on fossil fuels such as coal, petroleum and natural gas. Although the fossil-based fuels are satisfying the energy requirements of the world, the depletion of fossil energy reserves, the high demand for fossil fuels and the dependence on it have led researchers to search for sustainable and environmental-friendly energy sources. In this scenario, biodiesel is a sustainable alternative compared to diesel, due to its biodegradability, non-toxicity and low carbon content. Biodiesel can be a blended component in transportation fuels, as it demonstrates similar characteristics to petroleum diesel and has lower greenhouse gas (GHG) emissions [1]. Moreover, there are some concerns related to first-generation biodiesel (derived from food crops), such as the high cost of these oils, which accounts for about 70% of the total value of biodiesel production, as well as the competition with food markets, and the possibility of promoting soil degradation through the uncontrolled stimulation of energy crops [1,2]. Hence, second-generation biodiesel production has a considerable potential to reduce waste residues and GHG emissions by replacing fossil fuels. Waste cooking oils (WCO) are considered a promising alternative in biodiesel synthesis, due to their low cost, high availability and arise as possible alternatives to overcome the disadvantages of the traditional production processes [2].
Therefore, this study focuses on the research of producing biodiesel in a more sustainable way, namely the production of biodiesel from waste oils and the application of an ionic liquid as catalyst. Ionic liquids (ILs) are organic salts composed of cations and anions that can be used in biodiesel catalysis due to their attractive properties, such as good chemical stability, low vapor pressure, ability to be dissolved in a large range of inorganic and organic compounds and simple recovery process [3].
In this work, alkaline ILs, bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide [4] and choline hydroxide [5], were selected for the study of their performance for the catalysis of biodiesel production from WCO samples. The ILs were synthesized, characterised and used for the production of biodiesel batches. Operational parameters such as reaction time, reaction temperature, alcohol/oil molar ratio and catalyst dosage, will be optimized. IL recyclability will be assessed, and kinetic studies will be carried out to determine the activation energy of the transesterification reaction catalysed by the referred ILs.

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XXV
ENCONTRO

GALEGO
PORTUGUÉS DE
QUÍMICA

Cidade da Cultura- Edificio Cinc.
20 al 22 de noviembre de 2019
Santiago de Compostela - España

El Colegio Oficial de Químicos de Galicia, certifica que **Ana Carolina Lima** ha asistido al ***XXV Encontro Galego-Portugués de Química***, celebrado na Cidade da Cultura en Santiago de Compostela (España), del 20 al 22 de noviembre de 2019. y ha presentado dos Comunicaciones en formato Poster

Alkaline Imidazolium Ionic Liquid Evaluation for Catalysis of Biodiesel from Waste Cooking Oil

Para que conste y a los efectos oportunos, se expide el presente documento.

En Santiago, a 21 de Noviembre de 2019

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SOCIEDADE PORTUGUESA DE QUÍMICA

ASOCIACIÓN DE QUÍMICOS DE GALICIA

2ª Escola de Verão & Simpósio de Dupla Diplomação DD2019
2nd Double Diploma Summer School & Symposium DD2019

SYNTHESIS OF AN ALKALINE IMIDAZOLE IONIC LIQUID FOR THE CATALYSIS OF BIODIESEL PRODUCTION FROM WASTE OIL

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ABSTRACT

Fossil fuels are a primary energy resource that play a critical role in our daily activities. Currently, the provision of energy relies primarily on fossil fuels such as coal, petroleum and natural gas. Although the fossil-based fuels are satisfying the energy requirements of the world, the depletion of fossil energy reserves, the high demand for fossil fuels and the dependence on it has led researchers to search for sustainable and environmental-friendly energy sources. In this scenario, biodiesel is a sustainable alternative compared to diesel, due to its biodegradability, non-toxicity and low carbon content. Biodiesel can be a blended component in transportation fuels, as it demonstrates similar characteristics to petroleum diesel and has lower greenhouse gas (GHG) emissions [1]. Moreover, some concerns are related to first generation biodiesel (derived from food crops), such as the high cost of these oils, which accounts for about 70% of the total value of biodiesel production, as well as the competition with food markets, and the possibility of promoting soil degradation through the uncontrolled stimulation of energy crops [1,2]. Hence, second generation biodiesel production has a considerable potential to reduce waste residues and GHG emissions by replacing fossil fuels. Waste oils are considered a promising alternative in biodiesel synthesis, due to their low cost, high availability and arise as possible alternatives to overcome the disadvantages of the traditional production processes [4]. Therefore, this study focuses on the research of producing biodiesel in a more sustainable way, i.e., the production of biodiesel from waste oils and the application of an ionic liquid as catalyst. Ionic liquids are organic salts composed of cations and anions that can be used in biodiesel catalysis due to their attractive properties, such as good chemical stability, low vapor pressure, ability to be dissolved in a large range of inorganic and organic compounds and simple recovery process [3]. In this study, operational parameters such as reaction time and temperature, alcohol/oil molar ratio and catalyst dosage for the production of biodiesel from waste oil, catalyzed by bis-(3-methyl-1-imidazolium-)-ethlyene dihydroxide will be determined. Furthermore, kinetic studies will be carried out and different recovery strategies will be studied.

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B.3 VI Encontro de Jovens Investigadores do Instituto Politécnico de Bragança, December 2019.

Síntese e avaliação de um líquido iónico alcalino na produção de biodiesel

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Resumo
O biodiesel consiste em um biocombustível alternativo aos combustíveis fósseis, pois possui propriedades semelhantes às do diesel e apresenta biodegradabilidade, não toxicidade e baixo teor de carbono. Atualmente, a produção de biodiesel é realizada pela transesterificação de óleos comestíveis contendo triglicerídeos. O aproveitamento de óleos alimentares usados para a produção de biodiesel pode reduzir as preocupações relacionadas com o biodiesel de primeira geração, como o elevado custo dos óleos utilizados, a competição com o mercado alimentar e a possibilidade de degradação do solo. Devido ao seu baixo custo, alta disponibilidade e possíveis alternativas para superar as desvantagens dos processos de produção tradicionais, esses óleos alimentares usados são vistos como uma alternativa promissora na síntese de biodiesel. Assim, este trabalho centra-se no estudo da produção de biodiesel de uma forma mais sustentável, a partir de óleos alimentares usados e na aplicação de um líquido iónico (LI) como catalisador. O interesse nesses compostos decorre da sua pressão de vapor quase nula, por serem líquidos à temperatura ambiente e de propriedades como volatilidade baixa, alta estabilidade térmica e química e possibilidade de serem recuperados e reutilizados em novos ciclos reacionais. Nesta pesquisa, o LI di-hidróxido de bis-(3-metil-1-imidazólio)-etileno foi sintetizado e caracterizado, revelando bom caráter catalítico na transesterificação de amostras de óleo de girassol. Assim, o LI será aplicado na transesterificação de óleo de cozinha usado, e serão avaliados os efeitos de várias condições de reação, como tempo e temperatura da reação, razão molar álcool/óleo e dosagem do catalisador utilizado na preparação de biodiesel.

Palavras-chave: líquidos iónicos; catálise; biodiesel; óleo alimentar usado.

Alkaline ionic liquid synthesis and evaluation in biodiesel production

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Abstract
Biodiesel is an attractive biofuel to overcome energy depletion from fossil fuels since it has similar properties to diesel and exhibit biodegradability, non-toxicity and low carbon content. Currently, the production of biodiesel is done by the conversion of edible oils containing triglycerides through a transesterification reaction. However, concerns related to first-generation biodiesel such as the high cost of these oils, the competition with food markets, and the possibility of soil degradation made the utilization of waste oils in biodiesel production to be considered. These oils are considered as a promising alternative in biodiesel synthesis, due to their low cost, high availability and arise as possible alternatives to overcome the disadvantages of the traditional production processes. Therefore, this study focuses on the research of producing biodiesel in a more sustainable way, i.e., the production of biodiesel from waste oils and the application of an ionic liquid (IL) as catalyst. The interest in IL, is related to their near-zero vapor pressure and other properties such as their low volatility, high thermal and chemical stability, solvent properties and the possibility to be recovered and reused in new reaction cycles. In this research, the bis-(3-methyl-1-imidazolium)-ethylene dihydroxide (IMC_2OH) IL was synthesized and characterized, showing good catalytic character for the transesterification of sunflower oil samples. Thus, the IL will be applied in the transesterification of waste cooking oils, and the effects of different reaction conditions on the preparation of biodiesel, such as reaction time, reaction temperature, alcohol/oil molar ratio and catalyst dosage, will be assessed.

Keywords: ionic liquids; catalysis; biodiesel; waste cooking oil.

VI encontro de jovens investigadores

5 de dezembro de 2019

Certificado de comunicação

Certifica-se que **Ana Carolina Lima** apresentou no **VI Encontro de Jovens Investigadores**, que decorreu em Bragança, Portugal, no dia 5 de dezembro de 2019, a comunicação oral intitulada **Síntese e avaliação de um líquido iónico alcalino na produção de biodiesel**, tendo como autores:
Ana Carolina Lima, Maria Carolina Gomes, Paulo Miguel Brito, Ana Maria Queiroz and António Ribeiro

Bragança, 5 de dezembro de 2019

A Comissão de Organização,

Orlando Rodrigues
Presidente do Instituto Politécnico de Bragança

ipb INSTITUTO POLITÉCNICO DE BRAGANÇA