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Biodiesel production through esterification catalyzed by imidazolium based ionic liquids

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To my father Ridha

To my mother Amel

All my thanks!

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To all, my thanks!

Abstract

Due to the massive use of energy from non-renewable sources, and the associated environmental problems, there is a need to find viable alternatives to their replacement. The production of biodiesel as a substitute for diesel is one of the alternatives found.

Biodiesel consists of a mixture of, fatty acids methyl esters (FAMEs) and can be produced through two types of reactions: esterification of fatty acid mixtures and transesterification of vegetable oils and animal fats ; using conventional catalysts such as acids (sulfuric acid or sulfonic acid) or bases (sodium hydroxide or potassium hydroxide). Problems associated with the use of these catalysts have encouraged the search for more sustainable alternatives by introducing ionic liquids as catalysts because of their environmental and safety advantages and their recoverability and reuse.

The main objective of this study was to evaluate the recoverability of the ionic liquid 1-methylimidazolium hydrogen sulfate [HMIM][HSO_4] in the production of biodiesel through the esterification reaction of oleic acid in the presence of methanol at 4h, 65°C, with molar ratio methanol/oleic acid 1:10.The reaction yield was found to be 74% to 10% IL, 91% to 15% IL and 91% to 20% IL. These yields decreased to 44% (10% IL) with 4 cycles of recycling, 69% (15% IL) with 5 cycles of recycling and 69% (20% IL) with 4 cycles of recycling.

Keywords: Biodiesel; Esterification; Ionic liquids; Recovery; [HMIM][HSO_4]

Resumo

Devido ao uso massivo de energia proveniente de fontes não renováveis e aos problemas ambientais associados, é necessário encontrar alternativas viáveis à sua substituição. A produção de biodiesel como substituto para o diesel é uma das alternativas encontradas.

O biodiesel consiste numa mistura de ésteres metílicos de ácidos gordos livres (FAMEs) e pode ser produzido através de dois tipos de reações: esterificação de misturas de ácidos gordos e transesterificação de óleos vegetais e gorduras animais; utilizando catalisadores convencionais ácidos (ácido sulfúrico ou ácido sulfónico) ou básicos (hidróxido de sódio ou hidróxido de potássio). Os problemas associados ao uso desses catalisadores têm incentivado a procura de alternativas mais sustentáveis tais como os líquidos iónicos. Os líquidos iónicos apresentam vantagens a nível ambiental e de segurança, assim como a possibilidade de recuperação e reutilização.

O objetivo principal deste estudo foi avaliar a utilização do líquido iónico sulfato de hidrogénio de 1-metilimidazolio [HMIM] [HSO_4] na produção de biodiesel através da reação de esterificação do ácido oleico na presença de metanol com relação 1.10, com ácido oleico, 4h, 65°C, testando a sua recuperação e reutilização. Verificou-se que o rendimento da reação foi de 74% com 10% IL, 91% com 15% IL e 91% com 20% IL. Estes rendimentos diminuíram para 44% (10% IL) com 4 ciclos de reutilização, 69% (15% IL) com 5 ciclos e 69% (20% IL) com 4 ciclos de reutilização.

Palavras-chave: Biodiesel; Esterificação; Líquidos iónicos; Recuperação; [HMIM][HSO_4]

Résumé

En raison de l'utilisation massive de l'énergie provenant de sources non renouvelables et des problèmes environnementaux qui y sont associés, il est nécessaire de trouver des solutions de rechange viables à leur remplacement. La production de biodiesel comme substitut au diesel est l'une des alternatives trouvées.

Le biodiesel se compose d'un mélange d'esters méthyles d'acides gras libres, d'acides gras esters méthyles (FAME) et peut être produit par deux types de réactions : l'estérification des mélanges d'acides gras et la transesterification des huiles végétales et des graisses animales ; catalyseurs conventionnels : acides (acide sulfurique ou acide sulfonique) ou de bases (hydroxyde de sodium ou hydroxyde de potassium). Les problèmes associés à l'utilisation de ces catalyseurs ont encouragé la recherche d'alternatives plus durables en introduisant des liquides ioniques comme catalyseurs en raison de leurs avantages pour l'environnement et la sécurité, ainsi que de leur capacité de récupération et de leur réutilisation.

L'objectif principal de cette étude était d'évaluer le sulfate d'hydrogène 1-méthylimidazolium liquide ionique [HMIM][HSO_4] dans la production de biodiesel par la réaction d'estérification de l'acide oléique en présence de méthanol. A 65°C, 4h avec un ratio molair methanol, acid oleic 1:10 Le rendement de réaction s'est avéré être 74% à 10% IL, 91% à 15% IL et 91% à 20% IL. Ces rendements ont diminué à 44 % (10 % IL) avec 4 cycles de recyclage, 69 % (15 % D 'IL) avec 5 cycles de recyclage et 69 % (20 % IL) avec 4 cycles de recyclage.

Mots-clés: Production de biodiesel; L'estérification; Liquides ioniques; Récupération; [HMIM][HSO_4]

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Nomenclature

ABS	Aqueous biphasic systems
AC	Activated carbon
[BMIM]HSO_4	1-butyl-3-methyl imidazolium hydrogensulfate
[Emim]TfO	1-Ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide
FAME	Fatty Acid Methyl Ester
FFA	Free fatty acid
FTIR	Fourier Transform Infra-Red
GC-FID	Gas Chromatography with a Flame Ionization Detector
GHG	Greenhouse gas
HC	Hydrocarbon
[HMIM]HSO_4	1- methylimidazolium hydrogen sulfate
[Hnmm]OH	1-butyl-3-methyl morpholine hydroxide
[HO_3SPMIM]HSO_4	1-(3-sulfonic acid) propyl-3-methylimidazole hydrogen sulfate
KOH	Potassium hydroxide
NO_x	Nitric oxides
WCO	Waste cooking oil

INTRODUCTION

1.1 Background and motivation

Renewable energy has attracted more attention recently. The rising demand for fuels, mainly for the transportation sector, allied with an increasing concern for the environment, has been leading several researchers to look for alternatives to petroleum based energy sources. A wide range of raw materials can be used in the production of biodiesel. However, the use of cheap feedstock like oleic acid will be the greatest solution which usually features high levels of free fatty acids (FFA's), which can lead into problems to the classic process of production of biodiesel through alkaline esterification. These problems can be partially overcome by the use of ionic liquids (IL's) as catalyst that promotes the reactions of esterification of free fatty acids into biodiesel to obtain fatty acid methyl esters (FAME). One of the advantages of using ionic liquids as catalysts is that they can be recovered and reused for several cycles.

1.2 Objectives

The objectives of this work are:

- To study the biodiesel production by applying an acidic ionic liquid (1-methylimidazolium hydrogen sulfate, [HMIM]HSO_4) as catalyst to the esterification reactions between oleic acid and methanol.
- Assess the performance of the selected ionic liquid using different amounts of catalyst (10%, 15% and 20%).
- Recovery of the ionic liquid by washing with water as solvent using a ratio 1:3 between aqueous phase and water.

2. Biodiesel

2.1. Introduction

Energy is one of the most important resources for mankind and its sustainable development and today's energy crisis has become one of the most important problems confronting us. Fuels are of a great importance because they can be burned to produce significant amounts of energy. Many aspects of everyday life rely on fuels, in particular the transport of goods and people. The main energy resources come from fossil fuels such as petrol oil, coal and natural gas. The diesel production as an important source of energy is based essentially on fossil fuels that will be fractional distillated to produce diesel. Fossil fuel contributes 80% of the world's energy needs (Huang *et al.,* 2012). Most industries use diesel machines for their production processes. In the transportation sector, private vehicles, buses, trucks, and ships also consume significant amounts of diesel and gasoline. These situations contribute to a strong dependence of everyday life on fossil fuels. However, the growth of the population is not covered by domestic crude oil production. Alternative fuel must be technically appropriate, economically competitive, based on renewable raw materials, environmentally friendly and easily accessible; one of these fuels is a product of chemical modification of vegetable oils and animal fats by the reaction of transesterification, to produce biodiesel. (Stamenkovic *et al*., 2009)

In fact biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Indeed biodiesel has several advantages over traditional fuels obtained from other sources. Biodiesel is also known as fatty acid alkyl ester (FAAE). It is biodegradable, has less hazardous substances emitted from exhaust gases, and also can reduce the dependency on conventional diesel fuel. It can be produced via chemical reaction of feedstock, either vegetable oil or animal fat, in the presence of an alcohol. (Ullah *et al.*, 2015)

Biodiesel has being in use in many countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European nations. But the cost of biodiesel is the main hurdle to commercialization of the product. The logical way is to introduce cheaper feedstock into the industrial production, such as non-edible feedstock or waste cooking oil. So the used cooking oils are used as raw material, to decrease the cost of biodiesel and there are many advantages for using waste feed stock for biodiesel production: waste cooking oil is abundant, and is relatively inexpensive compared to other raw materials (Nurfitri *et al.*, 2013).Globally there are several ways to develop and improve the production of biodiesel for

direct use and blending: microemulsions, thermal cracking (pyrolysis) and transesterification. Studies that address the difference between each technology prove that transesterification, also called alcoholysis, is the best technique used until now. (Atabani *et al*., 2012)

In conclusion, biodiesel production is set to rise greatly in the coming years. Biodiesel offers the promise of numerous benefits related to energy security, economics, and expansion of the agriculture sector and reduction of polluting emissions.

2.2. Biodiesel advantages and disadvantages over other fuels

Here are presented some of the advantages and disadvantages of biodiesel:

Advantages: The production of biodiesel represents a good opportunity for the achievement of the European goals in terms of greenhouse gases (GHG) emissions reduction. It can protect the environment by reducing carbon dioxide, CO_2, sulfur dioxide, SO_2, carbon monoxide, CO emissions, and hydrocarbon, HC. Plants absorb CO_2, which is more than those discharged by the biodiesel combustion process. The use of biodiesel can turn more effective the reduction of the emissions of CO_2, protect the natural environment and maintain the ecological balance, compared to petro fuel. Furthermore the emissions of SO_2 in the combustion process of biodiesel are much lower than other fuels because of its lower sulfur content Thus, the use of biodiesel instead of normal diesel oil will effectively reduce acid rain, which represents serious threat to the environment and human infrastructure in forms of acidification of soil, surface and ground water forest and vegetation damage. Also, CO, HC and particulate matters will be less discharged, because ester compounds in biodiesel contains oxygen promoting clean burning. So as a result using biodiesel can also greatly decrease air pollution. But the greatly advantage of this fuel is that the raw materials used for production are natural and renewable. All these types of oils come from vegetables or animal fat, waste oil food, making it biodegradable and nontoxic (Huang *et al*., 2012). However, the high detergency of biodiesel can loosen debris in fuel systems that were formerly used for petroleum diesel and thus lead to a clogging of fuel filters. At higher concentrations, it can also degrade parts made of certain kinds of rubber commonly found in vehicles built before 1994 (Huang *et al*., 2012).Biodiesel is a good substitute of petro-diesel fuel due to its advantageous properties such as low sulfur content, lack of aromatics, higher lubricity and has also higher cetane number which is an index of flammability; so the flammability of biodiesel is better than petrodiesel. It can be used in existing conventional compression ignition engines and does not require any special modification to the engines. (Ullah *et al*., 2015)

Disadvantages: Biofuels are a key to the future energy development but they have on the other hand some disadvantages being currently the most important one the price that they are more expensive than fossil. Biodiesel fundamentally produced from comestible oil, could cause shortages of food supply and increase prices and reduce the fuel economy. Studies prove also that biodiesel is less suitable for use in low temperatures. Its use is restrictive in diesel powered engines. They are more likely than fossil diesel to attract moisture and caused increases in nitric oxide NO_x. (Viesturs *et al*., 2014)

2.3 Methods for biodiesel production

Researchers and scientists had developed different methods for biodiesel production from different biofuels. A brief review of these methods is presented here. In 1980, there was considerable discussion regarding use of vegetable oil as a fuel. Caterpillar Brazil, in 1980, used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. The advantages of vegetable oils as diesel fuel are: liquid nature-portability, availability and renewability. The disadvantages are higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains. Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. So they looked for others techniques: microemulsions, thermal cracking (pyrolysis), esterification and transesterification. (Maa *et al*., 1999)

2.3.1 Microemulsions

To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol and 1-butanol have been studied. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. (Maa *et al*., 1999)

2.3.2 Thermal cracking (Pyrolysis)

Pyrolysis, is by definition the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen, and cleavage of chemical bonds to yield small molecules. But pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petrofuel. (Maa *et al*., 1999)

2.3.3 Esterification

Esters have played a significant role in daily living and chemical industry, such as plasticizers, fragrance, adhesive and lubricants. The vast majority of esters can be prepared using esterification reaction in the chemical engineering industry. Esterification has acquired further improvement from the engineering side. Free fatty acids are carboxylic acids and they are converted to esters by a condensation reaction with alcohols, also known as esterification. The reaction can only be accomplished if the equilibrium is driven towards product formation, such as when there is an excess of reactants or one of the products is continuously removed from the reaction media. Figure 1 shows the general scheme for an esterification reaction catalyzed by acids. Carboxylic acid reacts with an alcohol, giving rise to water and an ester. (Zeng *et al*., 2011)

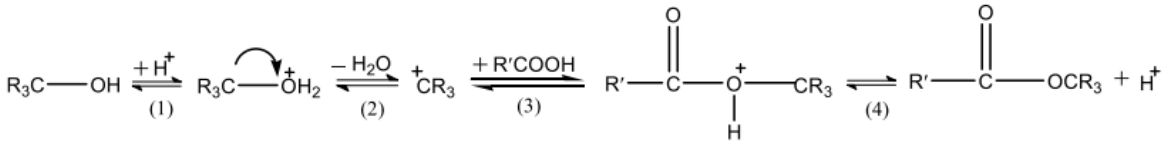


Figure 1. Mechanism for the esterification reaction. (Zeng *et al*., 2011)

2.3.4 Transesterification

Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. Transesterification consists of a number of consecutive, reversible reactions. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol. A mole of ester is

produced at each step (Atabania *et al*., 2012). Global equation of reaction of transesterification of triglycerides to obtain FAME and glycerol is showed in Figure 2.

Figure 2. Global equation of reaction of transesterification of triglycerides to obtain FAME and glycerol. (Atabania *et al*., 2012)

Acid-catalyzed transesterification: Acids used for transesterification include sulfuric, phosphoric, hydrochloric, and organic sulfonic acids. Although transesterification by acid catalysis is much slower than that by alkali catalysis, acid-catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid contents and more water. Some researchers reported that it was necessary to perform transesterification under an acidic condition when the oil component was a low grade material such as sulfur olive oil. In general, the ethyl esters of monounsaturated or short-chain fatty acids with 2% sulfuric acid should make good alternative fuels. (Fukuda *et al*., 2001)

Alkali-catalyzed transesterification: Alkalis used for transesterification include NaOH, KOH, carbonates, and alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Alkali-catalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst, and is thus most often used commercially (Fukuda *et al*., 2001). For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. And as a result the soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing is more difficult. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid-catalyzed transesterification can be used. The triglycerides can be purified by saponification (known as alkali treating) and then transesterified using an alkali catalyst (Maa *et al*., 1999)

Enzymatic transesterification by lipase: Although chemical transesterification using an alkali-catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several defects: it is energy intensive, the recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water requires treatment, and free fatty acids and water interfere with the reaction. But here extracellular and intracellular lipases are also able to effectively catalyze

the transesterification of triglycerides in either aqueous or non-aqueous systems, and studies prove that enzymatic transesterification methods can overcome the problems mentioned overhead. In particular, it should be noted that the product, glycerol, can be easily recovered without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to methyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of an alkaline one. (Fukuda *et al*., 2001)

2.4. Raw materials (waste cooking oils)

In spite of the favorable properties of biodiesel, economic reasons have been one of the major obstacles to its commercialization. Depending on the oil feedstock, it is reported that biodiesel is costly and its price is half times higher than that of petroleum diesel (Ullah *et al*., 2015). So the use of waste cooking oil will be the best solution because this oil would be thrown somewhere and this now it be used to produce biodiesel. However, during frying the oil can endure many chemical reactions such as polymerization, hydrolysis and oxidation owing to their reaction to light, heat and oxygen. As a result several different chemical compounds are produced such as dimer, polymer, oxidized triglycerides, diglycerides and fatty acids. In order to obtain a good yield of conversion of biodiesel, when waste cooking oils (WCO)are used as the raw material, the fatty acids of WCO should be converted to FAME (biodiesel) by esterification with methanol and a catalyst to minimize the WCO acid value followed by transesterification with the chosen catalyst (acid or base or enzyme catalyst). In order to achieve successful result of treated WCO transesterification by alkali catalyst, the feedstock is required to have lower FFA. So KOH has been suggested by many researchers as an alkali catalyst for the transesterification of oil having lower FFA. Figure 3 presents a diagram for the process of producing biodiesel using a waste cooking oil. (Ullah *et al*., 2015)

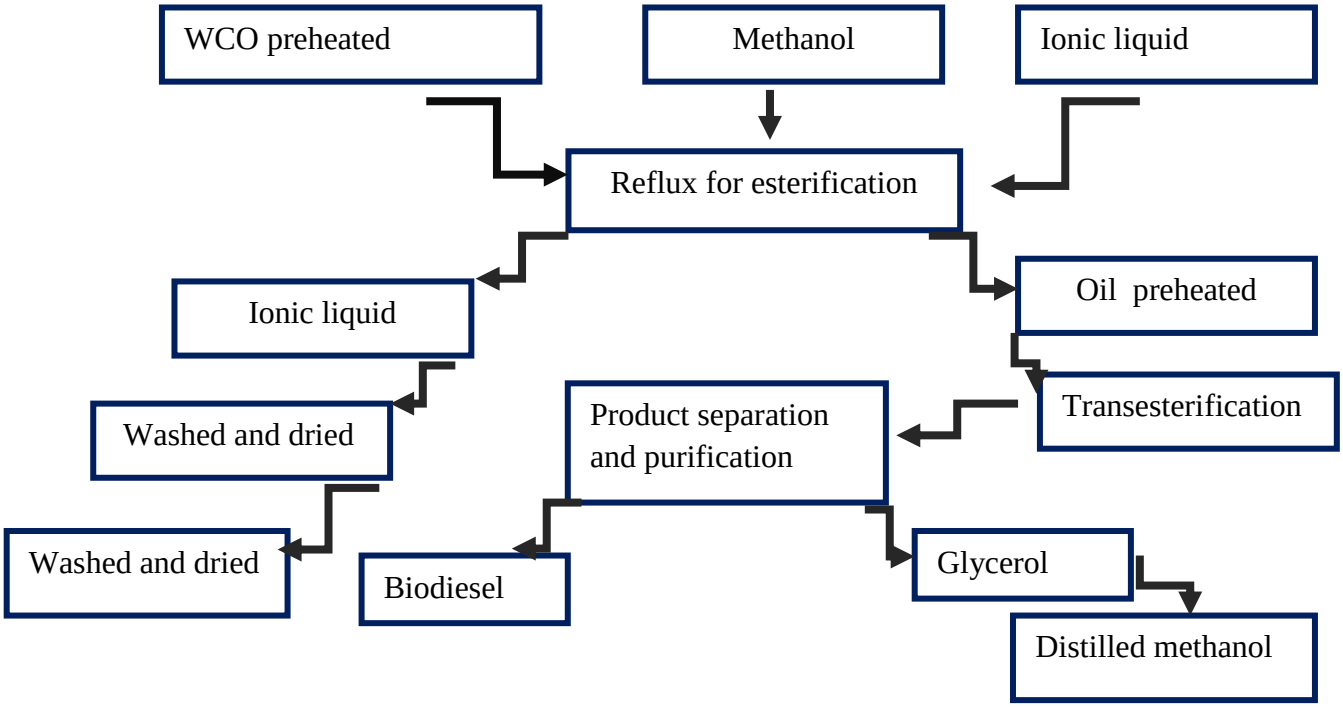


Figure 3. Schematic diagram of the biodiesel production from waste cooking oil. (Ullah *et al*., 2015)

An example of the mechanism of the reaction of triglycerides and methanol using ionic liquid 1- butyl- 3- methylimidazolium hydrogen sulfate, [BMIM]HSO_4, as catalyst in the production of biodiesel from waste cooking oil is presented in Figure 4. (Ullah *et al.*, 2015)

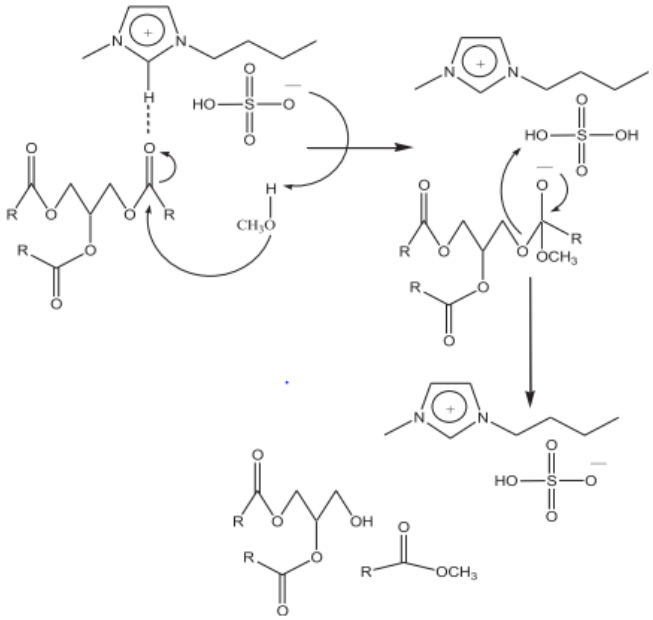


Figure 4. Mechanism reaction of triglycerides and methanol using ionic liquid [BMIM]HSO_4 (Ullah *et al*., 2015)

3. Ionic liquids as catalysts in biodiesel production

3.1. Brief introduction to ionic liquids

Ionic liquids are organic salts composed of anions and cations that are liquid at room temperature, in contrast to the simple inorganic salts that present high melting points. These compounds may be fluid at temperatures as low as -96°C because their ions although suffering attraction, are relatively large and present a difficult packing, not to mention delocalized charges (Andreani *et al*., 2012).. However, the ion attraction is sufficient for these compounds to have an almost null vapor pressure, meaning that there is almost no emission of volatile organic compounds during their use. Moreover, they can be colorless, non-flammable, have high catalytic activity, low viscosity, they are recyclable and are easily manipulated. The most interesting characteristic of ionic liquids is the possibility of designing a molecule aiming at a specific application or in order to obtain a certain set of properties such as melting point, viscosity, density, water solubility and selectivity. These compounds also have the ability to dissolve a variety of different substances, including polar and nonpolar organic compounds, inorganic and polymeric molecules due to their variable structure. Ionic liquids present the same interactions found in conventional organic solvents such as hydrogen bonding, dipole-dipole and van der Waals interactions, but also present ionic interactions such as mutual electrostatic attraction or repulsion between charged particles, which makes them very miscible with polar substances. Besides, the cation typically has an alkyl chain, the length of which determines its solubility in nonpolar fluids. Another advantage of these compounds is that there are at least 1 million binary ionic liquids, and 1018 ternary ionic liquids are potentially possible. In comparison, about 600 molecular solvents are currently in use .The ionic liquids allows the opportunity to choose how these compound will act in the reaction medium based on the cation and anion chosen, meaning that the choice of using a particular ionic liquid is conscious, and not random (Andreani *et al*., 2012).

Ionic liquids (IL‘s) as catalysts are able to reduce the number of reactions and purification steps, the production process consumes less energy and is more economically efficient. Besides that, IL’s are able to overcome some drawbacks associated with product separation and catalyst recycling in reactions where in most cases it was impossible to achieve 100% reaction conversion with 100% selectivity due to the thermodynamic limitations and the competition from parallel synthesis grows along with the prospect of developing environmentally safe green catalysts. For these reasons it is believed that the use of these salts in industrial green processes is promising provided that efficient recovery, separation of the product and reutilization are

possible. In other hand ionic liquids have been used in various fields such as organic synthesis, enzymatic catalysis Friedel-Crafts alkylations and acylations, Diels-Alder cycloaddition, aromatic nucleophilic substitutions, spectroscopy and electrochemistry, nanomaterials, polymerization and extraction and separation processes. Majority of studies focus on the use of ionic liquids in the process of oil transesterification, both as support or catalyst. When ionic liquids are used in the transesterification of triglycerides, the formation of a biphasic system at the end of the reaction appears because the ionic liquid is insoluble in the organic phase, and is a residue in the aqueous phase along with alcohol. The organic phase consists almost entirely of biodiesel. One of the advantages of these systems is the solubility presented by glycerol in a mixture of ionic liquid with methanol. Thus, glycerol is removed from the transesterification reaction and the equilibrium is attended to product formation, increasing the reaction yield. The ionic liquid/alcohol phase containing glycerol should be rinsed with water for 3 to 4 cycles to separate glycerol, which is then isolated in high purity. Comparatively, glycerol isolated from the traditional acidic or alkaline catalysis requires several purification steps to achieve same purity (Andreani *et al*., 2012).

3.2 Selected ionic liquid–methylimidazolium hydrogensulfate [HMIM]HSO_4

Studies proved that ionic liquids can act as catalysts for esterification reaction and transesterification and recently they received considerable attention due to their prospects for "green" catalysis. Besides, behaving as either solvent and/or catalyst in chemical processes drew attention not only in the area of academic but also in industrial field. Acidity/basicity of ionic liquids can be tuned for specific applications by choosing the cation/anion or its substitution pattern suitably (Ishak *et al*., 2017). Hydrogen sulfate ionic liquids as additives allow efficient conversion of carbohydrates into biofuels and as homogeneous catalysts they can be easily reactivated and recycled with activated carbon treatment. The structure of ionic liquid 1-methylimidazolium hydrogen sulfate is shown in Figure 5. (Shaterian *et al.*, 2013)

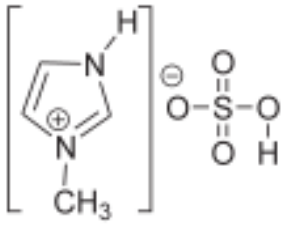


Figure 5. Structure of ionic liquid 1-methylimidazolium hydrogen sulfate (Shaterian *et al.*, 2013).

3.3 Recovery of ionic liquid techniques

As the cost of production of biodiesel is a major concern nowadays, the recyclability of catalysts used in the biodiesel process should be taken into account. Recycling of ionic liquids reduces the cost of biodiesel production and minimizes the disposal of ionic liquids as waste, thus reducing its environmental impacts. The recyclability of ionic liquids in transesterification reactions was carried out by almost all researchers in their reported studies (Ishak *et al*., 2017). The IL was recovered from the esterification (1st step) (Ullah *et al*., 2015) After completion of the esterification step the methanol was distilled off under vacuum, and cooled the mixture for a few moments and then centrifuge for 30 min, separates the IL from the bottom phase of the treated oil and then washed with hexane and ethyl acetate and then dried in vacuum for 4 h to reuse. ILs can be used for developing new processes that are technologically, environmentally and economically advantageous. However, ILs typically represents high costs. So, for an improvement in the economics, efficiency of the recycling and reuse of ILs are critical. Also, recovery of ILs is important to minimize the environmental concerns of the disposal, like biodegradation and toxicity (they can be mixed with other products). (Ullah *et al*., 2015)

For the recovery of ILs different methods are used and are summarized below.

3.3.1 Distillation

Distillation is considered as the simplest method for removal of the compounds having low boiling point and high thermal stability from ILs (due to their negligible vapor pressure). In this case catalysts and products were first removed from ILs media by decantation, filtration, extraction, and washing with water/organic solvents .After that, distillation can be used for recycling and reuse of IL's (Mai *et al*., 2014).

3.3.2 Extraction

Extraction of nonvolatile or thermal sensitive products from IL by liquid–liquid extraction thus allowing the recycling and reuse of ILs is also applied frequently. Many molecular solvents including water are immiscible with ILs. They make separated phases with ILs and can be used to extract or separate materials from IL solution. For example, hydrophilic products are easily extracted from hydrophobic ILs with water. Non-volatile or thermally sensitive hydrophobic

products are extracted from ILs by using organic solvents such as diethyl ether and hexane (Mai *et al*., 2014).

3.3.3 Adsorption

ILs can be recovered from aqueous solution by adsorption using absorbents. Although many studies have investigated the absorption of ILs onto solid supports such as activated carbon (AC), silica (SiO_2), alumina (Al_2O_3) and titanium oxide (TiO_2) (Mai *et al*., 2014).

3.3.4 Induced phase separation

Aqueous solution of ILs can form aqueous biphasic systems (ABS) by the addition of salts. This salting-out phenomenon provides an alternative pathway for recovering of ILs from aqueous effluents (Mai *et al*., 2014).

3.4. Use of biodiesel as a substitute for petrochemical diesel

For the determination of the quality of biofuels, the Standard EN 14214: 2003 is used. This discriminates the methods for the tests to be performed when determining the FAMEs. The quality of biofuels for car use is ensured and specified by the standards of European Committee for Standardization (CEN). (European Committee for Standardization. EN14214, 2003)

According to EU Directive 2009/30 / EC, biodiesel can be incorporated into diesel, at a maximum percentage of 7% (B7). In order to be able to incorporate this biofuel, it is necessary to guarantee its quality and homogeneity in order to comply with the technical specifications set forth in Decree-Law n°. 89/2008 of May 30. (Decree Law n ° 89/2008 of May 30)

For the year 2020, the European Union has determined that the percentage of biofuels used in road transport should be 10%. This target has been allocated to all EU countries. In Portugal, in 2017, the target for incorporation in energy content for biofuels, relative to the quantities of fuels determined for consumption should be about 7.5%, as stipulated by the State Budget in article 143 of Law no. 42/2016, of December 28. (Decree Law n ° 42/2016 of 28 December)

3.5. Production and consumption of biodiesel

The production of biodiesel through the use of vegetable oils and animal fats is the main goal stipulated for its production. However, in the year 2015, the production of biodiesel was mainly made from palm oil (29%), produced in large quantities in the east of Asia, followed by soybean oil (26%), produced in North and South America and last rapeseed oil (24%), produced mostly in Europe. (UFOP, 2017)

In 2015, about 49% of biodiesel production in the European Union (EU) derived from rapeseed oil, but the importation of other types of oil is still needed to suppress production needs. Normally, the type of oil purchased to suppress these needs varies according to the price each oil presents on the market. The most frequently acquired oil, palm oil, is from Southwest Asia, representing 14% of the biodiesel production in Europe. The use of used cooking oils represents about 17% of the production of biodiesel made in the EU. (UFOP, 2017)

The production of first generation biodiesel stimulates the potential sequestration of carbon by the consumption of CO_2 in the cultivation of oilseeds (Demirbas et *al*., 2009). The production of biodiesel decreases the dependence on oil and the importation of energy. This, because it enables the diversification of the national energy matrix and greater energy security to the country, as well as potentiates the export of biofuel. It is an alternative of great value for Portugal, for example, which does not have reserves of fossil fuel. (Zoreta, 2015)

The generation of employment and consequently income for the sectors of agriculture and industry are great social benefits that provide the production of biodiesel. In addition, investment in technologies and innovation are great strategies for the production of biofuel, which enables an increase in local and regional development. (Demirbas *et al.*, 2009)

3.6. Literature Review

Ionic liquids (ILs) have attracted much attention in both academics and industries as promising solvents for a diverse range of applications. However, actually there are few industrial processes employing ILs due to the high cost and low efficient use of ILs. The economic efficiency can be improved by recycling and reuse of ILs. In the last few decades, several studies can be found in literature focusing on the recovery and recycling of ILs. Table 1 summarizes some examples.

Liu *et al.*, 2013, studied the reaction between waste cooking oil and methanol, applying ionic liquids that depicted Brønsted acidity. They tested 10 different catalysts, including sulfuric acid.

The best result was obtained with the ionic liquid 1-(3-sulfonic acid)-propyl-3-methylimidazole hydrogen sulfate $[HO_3SPMIM]HSO_4$. The best conditions found were a reaction temperature of 120 °C, molar ratio between methanol and oil of 12:1, catalyst loading of 2 g and a reaction time of 8 h, leading to a 96% conversion. The same conditions were applied to acidic oils, which were prepared by adding oleic acid in different proportions to the raw material, and again, the conversion was over 90%. The recyclability was also addressed, and after 6 subsequent runs, no obvious reduction in the catalytic activity of the IL was detected.

Ding *et al.,* 2018, investigated the transesterification reaction of palm oil and methanol. Three synthesized ionic liquids were studied in order to determine their catalytic activity, followed by a single factor experiment to investigate the effect of several parameters on the reaction and then a RSM to optimize those factors. The best catalyst was the ionic liquid $[HSO_3$-BMIM$]HSO_4$ and the optimum condition was a methanol/oil ratio of 11:1, an ionic liquid dosage of 9.17 wt%, a microwave power of 168 W and a reaction time of 6.43h, leading to a yield of 98.9% .

Wei Xu *et al.*, 2015, compared the catalytic activity of the ionic liquid 1- methylimidazolium hydrogen sulfate, $[HMIM]HSO_4$, with the catalysts 1-butyl-3-methylimidazolium hydroxide [BMIM]OH, sodium hydroxide, and concentrated sulfuric acid. Although results showed that for the transesterification reaction between castor oil and methanol, the NaOH catalyst presented the best results, the ionic liquid 1-methylimidazolium hydrogen sulfate $[HMIM]HSO_4$ displayed a very similar trend. So, due to its advantages compared to the traditional catalyst, this ionic liquid was chosen for further studies. They run a screening test to study out of the 4 factors (temperature, time, and molar ratio methanol/oil and catalyst dosage) which factors were significant in the reaction conversion. They found that the reaction time was not an important factor and carried out the experiments with the remainder factors to the optimal conditions for the reaction, using a response surface methodology. They concluded that the optimal conditions were molar ratio methanol/oil of 6:1, reaction time of 4 h, temperature of 77ºC and a catalyst dosage of 12 wt%.

Ho Ha *et al.*, in 2007, tested 23 ionic liquids, the highest fatty acid methyl esters (FAMEs) production after 12 h at 50 °C was achieved in [Emim]TfO. The production yield of 80% was eight times higher compared to the conventional solvent-free system. It was around 15% higher than the FAMEs production system using tert-butanol as an additive. The optimum substrate

molar ratio of methanol to soybean oil for FAMEs production in1-ethyl-3-methyl imidazolium bis-(trifluoromethylsulfonyl) imide, [Emim] TfO was found to be 4:1.

Yassin Fathy *et al.*, 2015, proved 1-butyl-3-methyl imidazolium chloride, [BMIM]Cl to be a selective catalyst for the reaction of production of biodiesel from waste vegetable oil with a yield of 97% when used at 1:10, catalyst:oil ratio, for 8 h, at 55 °C. Operational simplicity, reusability of the used catalyst for 8 times at least, high yields and no saponification are the key features of this methodology.

Ren Qinggong *et al.*, 2014, used 1-butyl-3-methyl morpholine hydroxide, [Hnmm]OH for the catalysis of the synthesis of biodiesel from the reaction of methanol with soybean oil. The optimum reaction conditions were found as [Hnmm]OH amount of 4% (mass fraction), the methanol to soybean oil molar ratio of 8, temperature 70 °C and reaction time 1.5 h, the yield of biodiesel reached 97%, and exhibited high stability upon recycling: the yield of biodiesel was still more than 90% even after being reused for five times.

Ullah *et al.*, 2015, investigated the production of biodiesel from waste palm cooking oil using acidic ionic liquid as a catalyst. In this study, a two-step process esterification and transesterification was performed. The ionic liquid 1-butyl-3-methyl imidazolium hydrogensulfate,[BMIM]HSO_4, was found to be effective due to its longer side chain. The highest biodiesel yield was obtained with 5 wt.% [BMIM]HSO_4, methanol:oil ratio of 15:1, 60 min reaction time, at 160 °C, and agitation speed of 600 rpm, which reduced the waste cooking oil acidity to values lower than 1.0 mg KOH/g. The second step of transesterification catalyzed by KOH was carried out at 60°C, 1.0 wt% and 60 min of reaction time. The final yield was 95.65 wt% and after the sixth time of reusing this catalyst, the yield decreased to 83%.

Hafiidz *et al.*, 2012, used a Brφnsted acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4 as catalyst in the esterification of oleic acid into biodiesel. The optimum conditions for esterification of oleic acid were identified at methanol to oleic acid molar ratio of 9:1, catalyst loading of 3.4 wt%, reaction time 4 h, and reaction temperature 90°C, to maximum yield 91.6%.

The catalytic conversion of waste cooking oil (WCO) with high acid value (120.37 mg KOH/g) to biodiesel has been studied in low-cost SO_3H-functionalized quaternary ammonium ionic liquid as catalyst. Qi *et al.*, 2016, proved that the ionic liquid in their study was efficient in the catalysis of the simultaneous esterification and transesterification reactions of WCO and

methanol and it can be separated and reused for six cycles without any significant decrease in the biodiesel yield. Under the optimal reaction conditions (methanol/oil/IL molar ratio 10: 1: 0.063, 120°C, 1 h), and the maximum bio- diesel yield of 95% was achieved (Qi et al., 2016).

The esterification of oleic acid in the presence of magnetic ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM][$FeCl_4$]) at reaction temperature of 65 °C has been investigated. It was found that optimum responses for both yield and conversion were 83.4%, which can be achieved using molar ratio methanol/oleic acid of 22:1, catalyst dosage of 0.003 mol and reaction time at 36 h. Esterification of oleic acid at optimum condition using recycled [BMIM][$FeCl_4$] registered not much loss in catalytic activity after six successive runs (Hafiidz et *al*., 2014).

Table 1. Review of reaction conditions and number if ILs cycles found in literature.

Oil	Ionic Liquid	T(°C)	Time (h)	MeOH/oil ratio	Catalyst dosage	Yield (%) (FAME conversion)	Number of reaction cycles	References
Palm Oil	[HSO_3-BMIM]HSO_4	168	6.4	11:1	9.17 wt%	98.9	6	Ding *et al.*, 2018
Waste oil	[HO_3S-PMIM]HSO_4	120	8	12:1	2 g	96	[HO_3S-PMIM]HSO_4 IL could be reused six times without obvious decrease in its catalytic activity.	Liu *et al.*, 2013
Castor oil	[HMIM]HSO_4	77	4	6:1	12 wt%	89.9	[HMIM]HSO_4 was recycled 1, 2, 3, and 4times and the yield was 89.82%, 88.01%, 85.75%, and 82.32%.	Wei *et al.*, 2015
Soybean oil	[Emim]TfO	50	12	4:1	2 wt%	80	-	Ho Ha *et al.*,2007
Waste vegetable oils	[BMIM]Cl	55	8	10:1	5 g	97	8 times at least	Yassin Fathy *et al.*,2015
Soybean oil	[Hnmm]OH	70	1.5	8:1	4 wt%	97	5 times	Ren Qinggong *et al.*, 2014
Waste palm cooking oil	[BMIM]HSO_4	60	1	15:1	1.0 wt%	95.65	After the sixth time of reusing this catalyst, the yield decreased to 83%.	Ullah *et al.*, 2015
Oleic acid	[BMIM]HSO_4	90	4	9:1	3.4 wt%	91.6	-	Hafiidz *et al.*, 2012

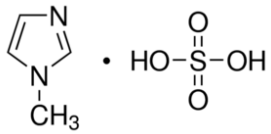
4. MATERIALS AND METHODS

For the experimental part 1-methylimidazolium hydrogen sulfate, [HMIM] HSO_4, ionic liquid was chosen in order to study the effect of its recovery. It was used in a set of 4 or 5 consecutive esterification reactions, using three different dosages of catalyst.

4.1. Reagents and materials

The reagents used for biodiesel production were at least analytical grade. The ionic liquid, 1-*methylimidazolium hydrogen sulfate* (+95%), the 37 component FAME mixture, Supelco 47885-U and heptadecanoic methyl ester, used as internal standard, were all obtained from Sigma Aldrich (Switzerland).The oleic acid, tech 90%, was obtained from ThermoFisher (Germany).All solvents, diethyl ether, ethanol, methanol, and n-heptane, were obtained from Carlo Erba (France).Anhydrous sodium sulfate, potassium hydroxide, sodium tetraborate and phenolphthalein , all analytical grade, were obtained from Panreac (Spain).

Table 2. Chemical structure and main properties of [HMIM][HSO_4]. Source: Sigma Aldrich catalog, 2019.

Chemical structure of [HMIM][HSO_4]	**Properties**	
	Nº. CAS:	681281-87-8
	Formula:	$C_4H_6N_2.H_2SO_4$
	MW (g/mol):	180.178

4.2. Equipment

Biodiesel production reaction was carried out using a 2-neek round-bottom 100 mL flask, dipped in a paraffin bath, using an automatic heating plate with magnetic agitation (VWR, model VMS-C4), connected to a reflux condenser. To separate the aqueous and organic phases, obtained after reaction, 100 mL glass separating funnels were used, as well as, a centrifuge (SIGMA, model 2-4). Drying was performed in a lab oven (SCIENTIFIC, series 9000) and a branstead lab line 3618-5 vacuum oven from Thermo Scientific All the masses were measured with a precision balance, ±0.0002 g (AE ADAM, model ADA 210/C). The FAME content in biodiesel samples was evaluated by gas chromatography with a flame ionization detector, GC-

FID, (SHIMADZU Nexis GC 2030) equipped with an autoinjector AOC-20i and an OPTIMA BioDiesel F capillary column (30m×0.25mm×0.23µm). The qualitative analysis of samples was carried out in an infrared spectroscopy system, FT-IR (Perkin Elmer, Model Spectrum Two) in transmission mode using ATR cell and the SPECTRUM10 software from Perkin Elmer.

4.3. Experimental methodology

4.3.1. Esterification reaction procedure

The esterification reaction was performed by adding ionic liquid, oleic acid and methanol, in this order, using previous defined amounts, in a 100 mL reaction vessel. The vessel, containing the mixture, was immersed in a bath, previously heated to a selected temperature, under automatic agitation and connected to a reflux condenser (Roman, 2018). The schematic of the experimental assembly is shown in Figure 6.

Figure 6. The experimental assembly used for esterification reactions.

At the end of reaction, the vessel was removed from the bath and let cool down to room temperature. Then, the product was measured, transferred to glass tubes and centrifuged (3000 rpm for 50 minutes). After separation of the organic and aqueous phases, the biodiesel phase was heated to evaporate both residual water and methanol in a drying oven and both phases were stored at 4 ºC for further analysis (see Figure 7).

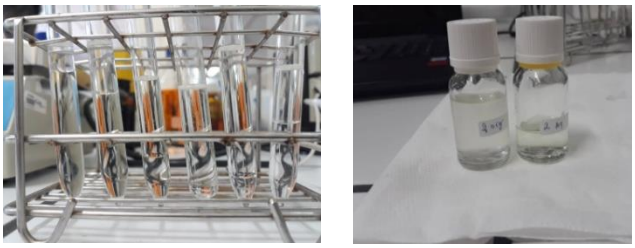


Figure 7. Separation and storage of organic and aqueous phases.

4.3.2. Determination of biodiesel samples acidity

The organic phase (biodiesel) acidity was measured, accordingly to EN 14104 standard (EN 14104, 2003) using an alcoholic potassium hydroxide solution. For this measurement, 1g of biodiesel sample was transferred to an Erlenmeyer containing 25 mL of diethyl ether/ethanol 1:1 (v/v) solvent mixture and 5 drops of phenolphthalein solution. The organic phase was then titrated with a standard KOH solution. The acid value is given in terms of mg of KOH/g biodiesel as presented in Equation 1,

$$\text{Acid value , AV (mg de KOH /g biodiesel)} = \frac{V_{KOH} \times C_{KOH} \times MW_{KOH}}{m_{biodiesel}} \quad (1)$$

Where V_{KOH} is the volume (mL) of potassium hydroxide used in the titration, C_{KOH} is the concentration (mol/L) of potassium hydroxide solution, MW_{KOH} is the molar weight of potassium hydroxide (g/mol), and $m_{biodiesel}$ is the mass (g) of biodiesel sample. The acidity value (AV) was measured in triplicate for each biodiesel sample. The conversion, measure in terms of acidity decrease, was calculated by comparing the acidity of the raw material, with the average acidity of the biodiesel samples, using Equation 2,

$$Conversion, X(\%) = \frac{AV_{oleic\ acid} - AV_{biodiesel}}{AV_{oleic\ acid}} \times 100 \quad (2)$$

4.3.3. Determination of fatty acid methyl esters content in biodiesel samples

Gas chromatography with a flame ionization detector (GC-FID), see Figure 8,was used to measure the fatty acid methyl esters (FAME) content in biodiesel samples, in compliance with the European Standard EN14103 (EN14103, 2003). After the determination of the acidity, the organic phase was dried using an oven at 110 ºC for 5 h. The biodiesel samples were then prepared for gas chromatography analysis. Aliquots of 250 mg were transferred to 10 mL vials

and 5 mL of methyl heptadecanoate (used as internal standard) solution with a concentration of 10 mg/mL was added. Then, small quantities of anhydrous sodium sulfate were added to remove the remaining moisture present in the sample. The flask was then closed and stirred appropriately, the salt was decanted and 1 μL of the solution was withdrawn into a 2 mL vial for analysis. The GC analysis were carried out using the following operating conditions: helium flow-rate of 1 mL/min, initial oven temperature of 50 °C maintained for 1 min, then a temperature ramp at 25 °C/min to 200 °C, and then a second ramp at 3 °C/min until 230 °C. The final temperature was maintained for 23 min, for a total running time of 20 min. The injector was operated with a temperature of 250 °C, the split ratio was 1:25, and the detector temperature was 250 °C. The identification of all FAME compounds was done using optima biodiesel F column was done by comparing the retention times of the Supelco 37 FAME compound mix analysis, obtained in the GC Shimadzu system, with the published results by Supelco for the same FAME mixture using a DB-Wax column.

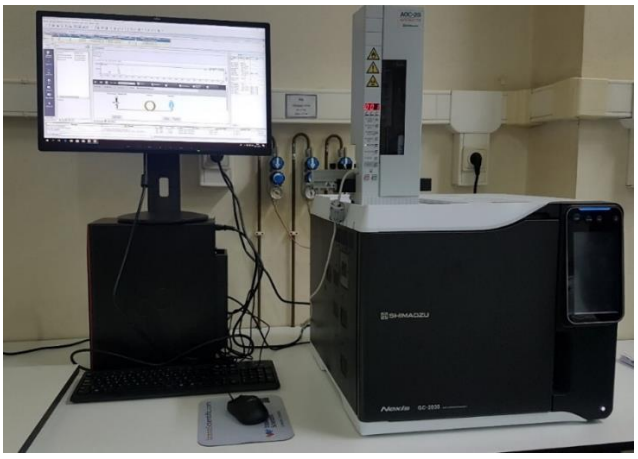


Figure 8. GC-FID equipment used to measure the content of FAMEs in biodiesel samples.

The GC-FID chromatogram obtained for the Supelco 37 FAME compound mix is presented in Figure 9.

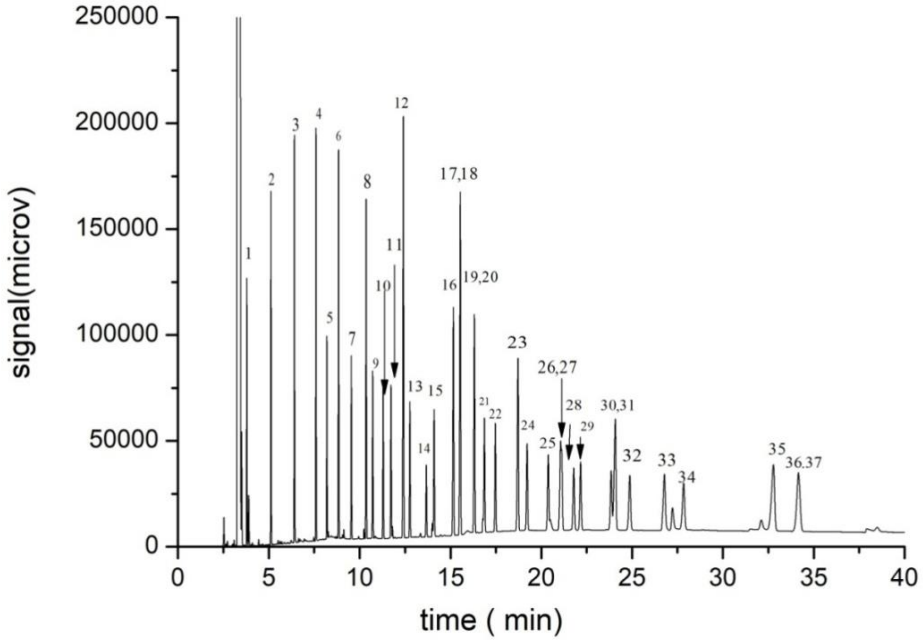


Figure 9. Chromatographic analysis obtained by GC-FID chromatogram for the 37 compound FAME mix obtained using Shimadzu equipment, and an OPTIMA Biodiesel F column.

The experimental identification results are presented in Table 3. After identification of all 37 FAME compounds, the individual and the total chromatographic areas of FAMEs were used to quantify the FAME content present in biodiesel samples using Equation 3, according to EN14103. (EN14130, 2003)

$$C(\%) = \frac{(\sum A_{FAME} - A_{IS})}{A_{IS}} \times \frac{m_{IS}}{m_{biodiesel}} \times 100 \qquad (3)$$

where

ΣA_{FAME} is the total peak area from the methyl ester C14:0 to C24:1, A_{IS} is the peak area corresponding to methyl heptadecanoate, m_{IS} is the mass of the methyl heptadecanoate solution, and $m_{biodiesel}$ is the mass of biodiesel.

Table 3. Identification and elution order for all compounds, present in the Supelco standard 37 FAME mix, using the GC-FID Shimadzu system.

Elution order	Compound name	Compound ID	Retention time (min)
1	Butyric acid methyl ester	C4:0	3.789
2	Caproic acid methyl ester	C6:0	5.118
3	Caprylic acid methyl ester	C8:0	6.409
4	Capric acid methyl ester	C10:0	7.594
5	Undecanoic acid methyl ester	C11:0	8.197
6	Lauric acid methyl ester	C12:0	8.84
7	Tridecanoic acid methyl ester	C13:0	9.544
8	Myristic acid methyl ester	C14:0	10.356
9	Myristoleicacd methyl ester	C14:1	10.719
10	Pentadecanoic acid methyl ester	C15:0	11.291
11	cis-10-Pentadecanoic acid methyl ester	C15:1	11.725
12	Palmitic acid methyl ester	C16:0	12.405
13	Palmitoleic acid methyl ester	C16:1	12.763
14	Heptadecanoic acid methyl ester	C17:0	13.667
15	cis-10-Heptadecanoic acid methyl ester	C17:1	14.096
16	Stearic acid methyl ester	C18:0	15.157
17,18	Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	15.537
19,20	Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	16.312
21	gamma-Linolenic acid methyl ester	C18:3n6	16.863
22	Linolenic acid methyl ester	C18:3n3	17.467
23	Arachidic acid methyl ester	C20:0	18.711
24	cis-11-Eicosenoic acid methyl ester	C20:1	19.21
25	cis-11,14-Eicosadienoic acid methyl ester	C20:2	20.463
26, 27	cis-8,11,14-Eicosatrienoic acid methyl ester, Heneicosanoic acid methyl ester	C21:0	21.127
28	cis-11,14,17-Eicosatrienoic acid methyl ester	C20:3n3	21.798
29	Arachidonic acid methyl ester	C20:4n6	22.175
30,31	cis-5,8,11,14,17-Eicosapentaenoic acid methyl ester, Behenic acid methyl ester,	C20:5n3 C22:0	24.081
32	Erucic acid methyl ester	C22:1	24.879
33	cis-13,16-Docosadienoic acid methyl ester	C22:2	26.784
34	Tricosanoic acid methyl ester	C23:0	27.843
35	Lignoceric acid methyl ester	C24:0	32.784
36,37	cis-4,7,10,13,16,19-Docosahexanoic acid methyl ester, Nervonic acid methyl ester	C22:6n3 C24:1	34.159

4.3.4. Recovery of ionic liquid

The recovery of ionic liquid was performed in order to measure the number of times that the catalyst could be used in the reaction without significantly losing in its catalytic capacity. This study of recovery was performed for esterification reactions using the [HMIM][HSO_4]ionic liquid in three different contents,10%, 15% and 20%, an oleic acid: methanol molar ratio of 1:10, a reaction time of 4 hours and a reaction temperature of 65 °C. The recovery of ionic

liquid was also studied using two different methods for drying the aqueous samples: in the oven at 110°C, or in a vacuum oven at 60°C or 70 °C. After washing with the adequate solvent (water) with a mass ratio 1:3, the sample is decantated for 24 h in a funnel to separate the aqueous phase from the impurities, which are residues of oleic acid that do not react, or FAME's that migrated from the organic phase. The upper phase contains biodiesel and non-reacted oleic acid, while the lower phase contains ionic liquid, methanol and water that after drying through the two methods previously referred, will be transferred to a flask and stored to be used in other reaction cycle.

Figure 10. Phases separation after reaction using decantation funnel.

4.3.5. Structural analysis using FT-IR infrared spectroscopy

The FTIR analysis is a technique used in the qualitative analysis of compounds present in a sample by identifying the vibrations of each of its functional groups. The analysis was performed in an infrared spectroscopy system. The infrared spectra were obtained by performing several scans in a range between 4000 and 450 cm^{-1}. The FT-IR system is presented in Figure 11.

Figure 11. FT-IR spectroscopy equipment (PerkinElmer, model Spectrum Two) with an ATR cell.

5. RESULTS AND DISCUSSION

5.1. Objectives of the analysis

The results presented below intend to determine the capacity of the ionic liquid [HMIM][HSO_4] to act as a catalyst in the esterification reaction of oleic acid with methanol. Roman, 2018, conducted a previous study where she studied the catalytic activity of 1-methyl imidazolium hydrogen sulfate, [HMIM][HSO_4], in the following experimental conditions: 6 h reaction time, reaction temperature of 90ºC, catalyst loading of 10 wt% and a methanol/oleic acid ratio of 10:1. The ionic liquid in her study was selected as a good option as a catalyst presenting the second best result with a conversion of 88.52 % (in terms of acidity reduction), for the esterification reaction of oleic acid with methanol for production of biodiesel.

5.2. The characterization of the feedstock

The characterization of oleic acid as feedstock was performed by GC-FID analysis. The objective of this study was to determine the specific composition of the oleic acid sample, by derivatizing the acids present with the corresponding methyl esters and then identifying and quantifying them by GC using the internal standard method. Since the purity of the oleic acid used as feedstock is around 90%, it is contemplated that the ester found in the greatest amount after the derivatization procedure is the oleic acid methyl ester. In fact, palmitic acid methyl ester (C16:0), oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), linoleic acid, linoleic acid methyl ester C18:2(c+t) and heptadecanoic acid methyl ester, (C17:0) corresponding to the internal standard, making up a total as percentage of FAMEs of 89.2% in Table 4 is displayed the FAME content for each of the identified esters (ID).

Table 4. FAME content for each of the identified esters (ID).

Compound name	**Compound ID**	**FAME (%)**
Palmitic acid methyl ester	C16:0	1.6%
Stearic acid methyl ester	C18:0	0.7
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	85.2%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	1.7%
Sum	-	89.2%

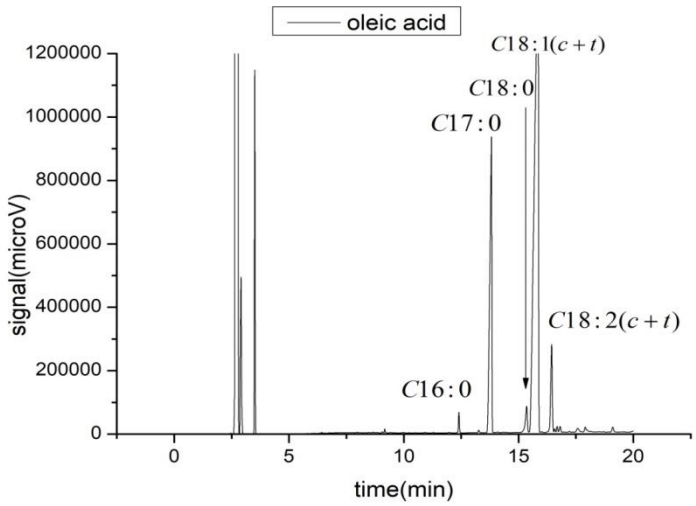


Figure 12. Chromatogram obtained after the derivatization of FAME from OA.

The acid value (AV) for the oleic acid as raw material was determined in triplicate and the results obtained are presented in Table 5.

Table 5. Acid value of oleic acid.

Assay	**m** of biodiesel (g)	**V KOH** (mL)	**AV** (mg KOH/g OA)
1	1.0844	49.10	181.20
2	1.0859	49.20	181.32
3	1.0641	47.90	180.14

For the OA sample, the average acid value determined was 180.89 mg KOH/g OA.

5.3. Experimental conditions

The detailed reactions conditions temperature, time, mass of oleic acid, mass of ionic liquid, volume of methanol, amount of catalyst are summarized in Table 6 for 10% content of IL, Table 7 summarizes the reaction conditions with 15% content of IL, and finally Table 8 presents the reactions condition of 20% amount of catalyst.

Table 6. Reactions conditions with amount 10% of [HMIM]HSO_4.

N° of cycle	Reaction	m[HMIM] HSO_4 (theo), g	m [HMIM] HSO_4 (exp), g	m of OA (theo), g	m of OA (exp), g	m of MeOH (theo), g	VMeOH (mL)	OA / MeOH , time, T(°C), % IL
0	1.1	1.0000	1.0250	10.0000	10.3120	11.3512	14.37	1:10,4h,65°C,10%
1	2.1	0.7541	0.7541	7.5410	7.4491	8.5600	10.84	1:10,4h,65°C,10%
2	3.1	0.6340	0.6189	6.3400	6.4015	7.1967	9.11	1:10,4h,65°C,10%
3	4.1	0.4538	0.4522	4.5380	4.5788	5.1512	6.52	1:10,4h,65°C,10%

Table 7. Reactions conditions with 15% amount of [HMIM]HSO_4.

N° of cycle	Reaction	m [HMIM] HSO_4 (theo), g	m [HMIM] HSO_4 (exp), g	m of OA (theo), g	m of OA (exp), g	m of MeOH (theo), g	VMeOH (mL)	OA / MeOH , time, T(°C), % IL
0	1.2	1.5000	1.5393	10.0000	10.1048	11.3512	14.37	1:10,4h,65°C,15%
1	2.2	1.3933	1.2871	8.5807	8.7019	9.7401	12.33	1:10,4h,65°C,15%
2	3.2	1.1594	1.0945	7.2967	7.5551	8.2826	10.48	1:10,4h,65°C,15%
3	4.2	0.9988	0.9531	6.3540	6.5209	7.2126	9.13	1:10,4h,65°C,15%
4	5.2	0.7566	0.7068	4.7120	4.9328	5.3487	6.77	1:10,4h,65°C,15%

Table 8. Reactions conditions with 20% amount of [HMIM]HSO_4.

N° of cycle	Reaction	[HMIM] HSO_4 (theo), g	m [HMIM] HSO_4 (exp), g	m of OA (theo), g	m of OA (exp), g	m of MeOH (theo), g	VMeOH (mL)	OA / MeOH , time, T(°C), % IL
0	1.1	2.0000	2.0486	10.0000	10.2252	11.3512	14.37	1:10,4h,65°C,20%
1	2.1	1.6911	1.5494	7.7470	7.8560	8.7938	11.13	1:10,4h,65°C,20%
2	3.1	1.5211	1.4836	7.4180	7.9429	84203	10.66	1:10,4h,65°C,20%
3	4.1	1.4002	13605	6.8025	79429	7.7217	9.77	1:10,4h,65°C,20%

5.4. GC-FID: Determination of FAMEs content in biodiesel samples

The evolution of the esterification reaction was quantified in terms of the content of fatty acid methyl esters (FAME's) produced, the chromatogram of GC-FID analyses of all the reactions done are showed below .For the preparation of the samples to be analyzed were weighted 250 mg of sample for a 10 mL vial and 5 mL of solvent were added. Tables 9 to 21 show the results of FAME's content for each reaction.

*GC results for the load of 10% of IL

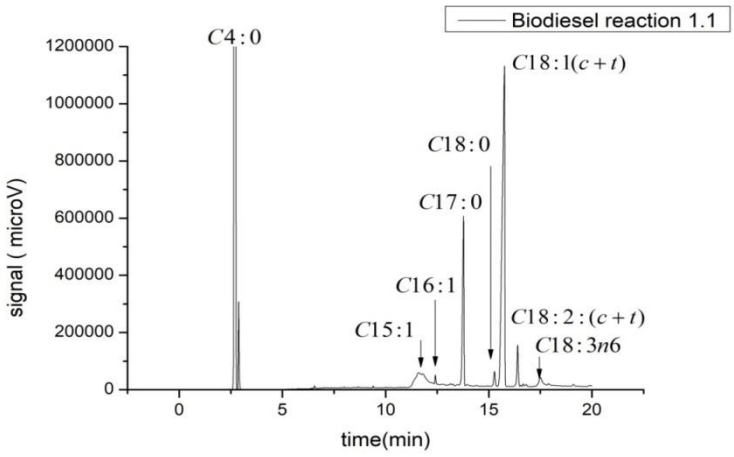


Figure 13. Chromatogram obtained after the derivatization of FAME from biodiesel reaction.

From the GC-FID analysis for reaction 1.1 the main fatty acids constituting the analyzed are 0.31% of cis-10-Pentadecanoic acid methyl ester C15:1, 0.12% of palmitoleic acid methyl ester, C16:1, 1.91% of stearic acid methyl ester C18:0, 66.86% of oleic acid methyl ester, Elaidic acid methyl ester C18:1(c+t),3.80% of linoleic acid methyl ester, Linolelaidic acid methyl ester C18:2(c+t),0.06 % of γ-Linolenic acid methyl ester C18:3n6. In relation to the internal standard, biodiesel from reaction 1.1 shows a total percentage of FAMEs of 73.64%. Table 9 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel from reaction 1.1.

Table 9. FAME content for each of the identified esters (ID) for reaction 1.1.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	0.31%
Palmitoleic acid methyl ester	C16:1	0.12%
Stearic acid methyl ester	C18:0	1.91%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	66.86%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	3.80%
gamma-Linolenic acid methyl ester	C18:3n6	0.06%

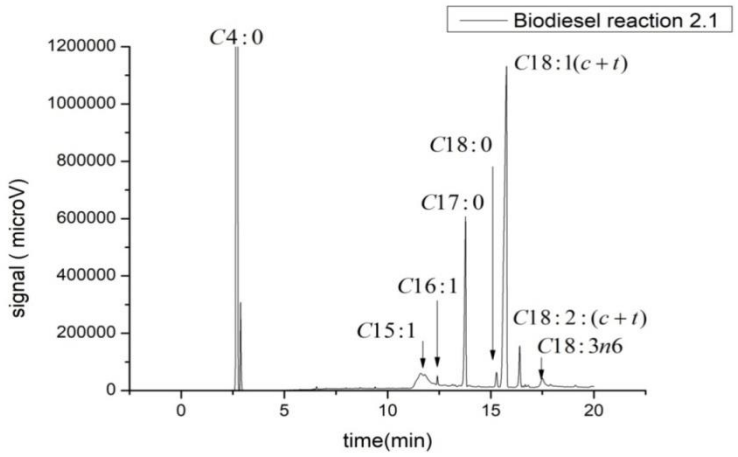


Figure 14. Chromatogram obtained after the derivatization of FAME from biodiesel reaction 2.1.

From the GC-FID analysis for reaction 2.1, the main fatty acids constituting the analyzed are 0.05% of cis-10-Pentadecanoic acid methyl ester C15:1, 0.17% of palmitoleic acid methyl ester C16:1, 0.57% of stearic acid methyl ester C18:0, 55.21% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 4.36% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t), 0.06% of gamma-linolenic acid methyl ester C18:3n6. Corresponding to the internal standard, biodiesel reaction 2.1 makes up a total percentage of FAMEs of 61.49%. Table 10 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 2.1.

Table10. FAME content for each of the identified esters (ID) for reaction 2.1.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	0.05%
Palmitoleic acid methyl ester	C16:1	0.17%
Stearic acid methyl ester	C18:0	0.57%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	55.21%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	4.36%
Gamma-Linolenic acid methyl ester	C18:3n6	0.06%

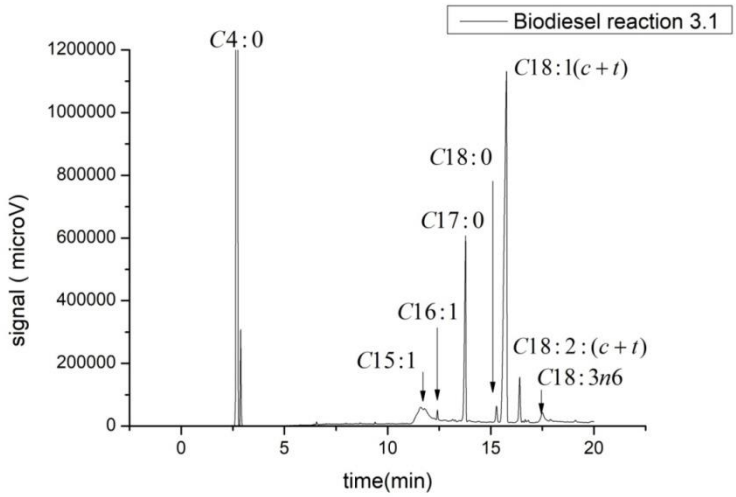


Figure 15. Chromatogram obtained after the derivatization of FAME from biodiesel reaction 3.1.

From the GC -FID analysis for reaction 3.1, the main fatty acids constituting the analyzed are 1.72% of cis-10-Pentadecanoic acid methyl ester C15:1, 1.46% of palmitoleic acid methyl ester C16:1, 2.12% of stearic acid methyl ester C18:0, 49.97% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 0.24% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t), 0.09% of gamma-linolenic acid methyl ester C18:3n6. Corresponding to the internal standard, biodiesel reaction 1.1 makes up a total percentage of FAMEs of 55.51%. Table11 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 3.1.

Table 11. FAME content for each of the identified esters (ID) for reaction 3.1.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	1.72%
Palmitoleic acid methyl ester	C16:1	1.46%
Stearic acid methyl ester	C18:0	2.12%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	49.97%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.24%
Gamma-Linolenic acid methyl ester	C18:3n6	0.09%

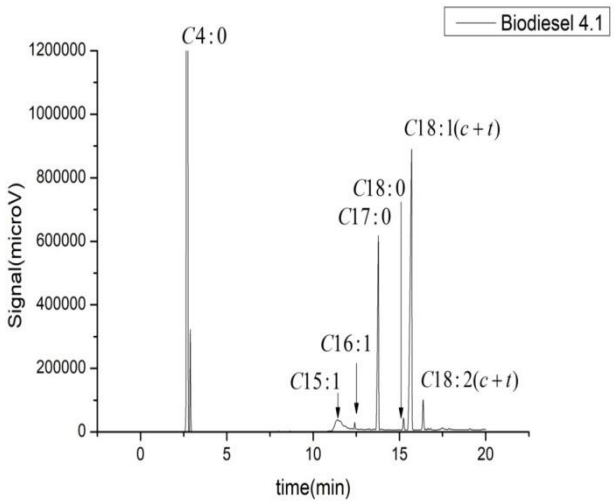


Figure 16. Chromatogram obtained after the derivatization of FAME from biodiesel reaction 4.1.

From the GC-FID analysis for reaction 4.1 the main fatty acids constituting the analyzed are: 0.7% of palmitoleic acid methyl ester (C16:1), 1.4 % of stearic acid methyl ester 43.6% of oleic acid methyl ester, elaidic acid methyl ester C18:1 (c+t), 0.2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2 (c+t). Corresponding to the internal standard, biodiesel reaction 4.1 makes up a total percentage of FAMEs of 45.31%. Table 12 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 4.1.

Table 12. FAME content for each of the identified esters (ID) for reaction 4.1.

Compound name	Compound ID	FAME (%)
Palmitoleic acid methyl ester	C16:1	0.7%
Stearic acid methyl ester	C18:0	1.4%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	43.6%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.2%

*GC results for 15% load of IL

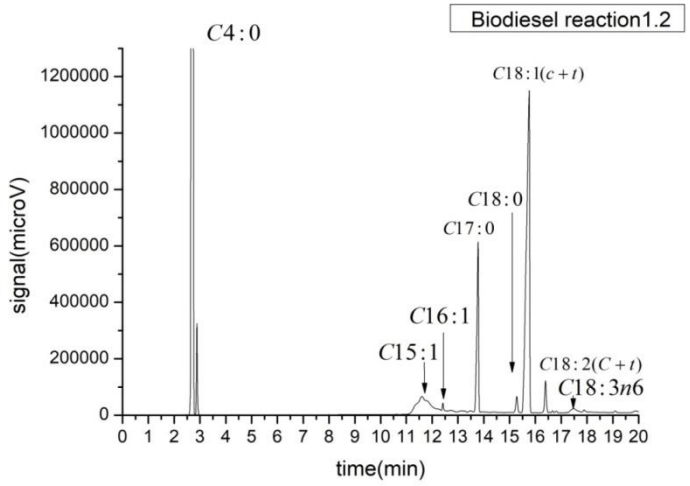


Figure 17. Chromatogram obtained after the derivatization of FAME from biodiesel reaction 1.2.

From the GC-FID analysis for reaction 1.2, the main fatty acids constituting the analyzed are 16% of cis-10-Pentadecanoic acid methyl ester C15:1, 1.8% of palmitoleic acid methyl ester C16:1, 2.5 % of stearic acid methyl ester C18:0, 69 % of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 0.2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t), 2.2% of gamma-linolenic acid methyl ester C18:3n6. Corresponding to the internal standard, biodiesel reaction 1.2 makes up a total percentage of FAMEs of 91.26%. Table 13 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 1.2.

Table 13. FAME content for each of the identified esters (ID) for reaction 1.2.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	16.0%
Palmitoleic acid methyl ester	C16:1	1.8%
Stearic acid methyl ester	C18:0	2.5%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	69.0%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.2%
gamma-Linolenic acid methyl ester	C18:3n6	2.2%

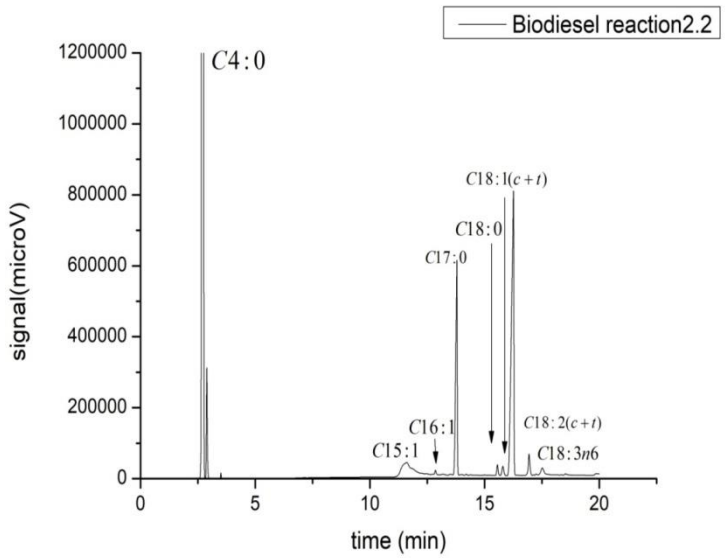


Figure 18. Chromatogram obtained after the derivatization of FAME from biodiesel reaction 2.2.

From the GC-FID analysis for reaction 2.2, the main fatty acids constituting the analyzed are 9.9% of cis-10-Pentadecanoic acid methyl ester C15:1, 0.7% of palmitoleic acid methyl ester C16:1, 0.9 % of stearic acid methyl ester C18:0, 38.7 % of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 2.2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t), 1% of gamma-linolenic acid methyl ester C18:3n6. Corresponding to the internal standard, biodiesel reaction 2.2 makes up a total percentage of FAMEs of 53.59%. Table 14 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 2.2.

Table14 .FAME content for each of the identified esters (ID) for reaction 2.2

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	9.9%
Palmitoleic acid methyl ester	C16:1	0.7%
Stearic acid methyl ester	C18:0	0.9%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	38.7%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	2.2%
gamma-Linolenic acid methyl ester	C18:3n6	1%

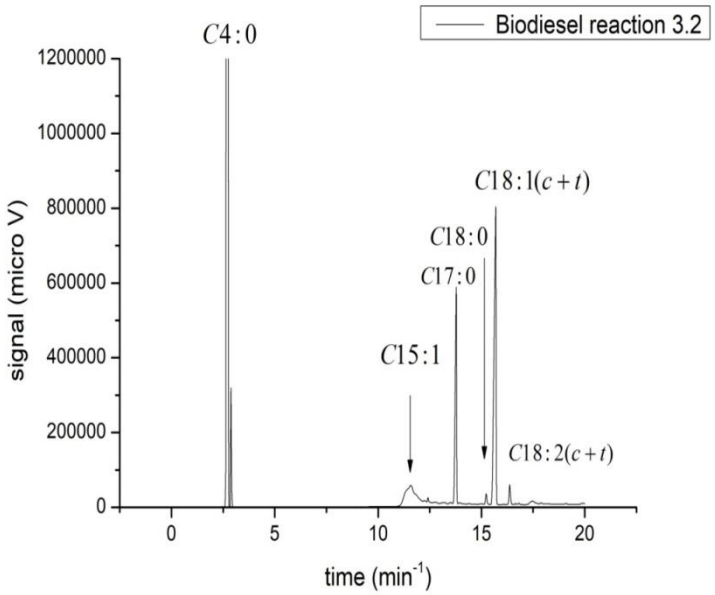


Figure 19. Chromatogram obtained after the derivatization of FAME from biodiesel reaction 3.2.

From the GC-FID analysis for reaction 3.2, the main fatty acids constituting the analyzed are 15% of cis-10-Pentadecanoic acid methyl ester C15:1, 1.3 % of stearic acid methyl ester C18:0, 38.4 % of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 0.1% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). Corresponding to the internal standard, biodiesel reaction 1.1 makes up a total percentage of FAMEs of 54.40%. Table 15 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 3.2.

Table 15. FAME content for each of the identified esters (ID) for reaction 3.2.

Compound name	**Compound ID**	**FAME (%)**
cis-10-Pentadecanoic acid methyl ester	C15:1	15.0%
Stearic acid methyl ester	C18:0	1.3%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	38.4%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.1%

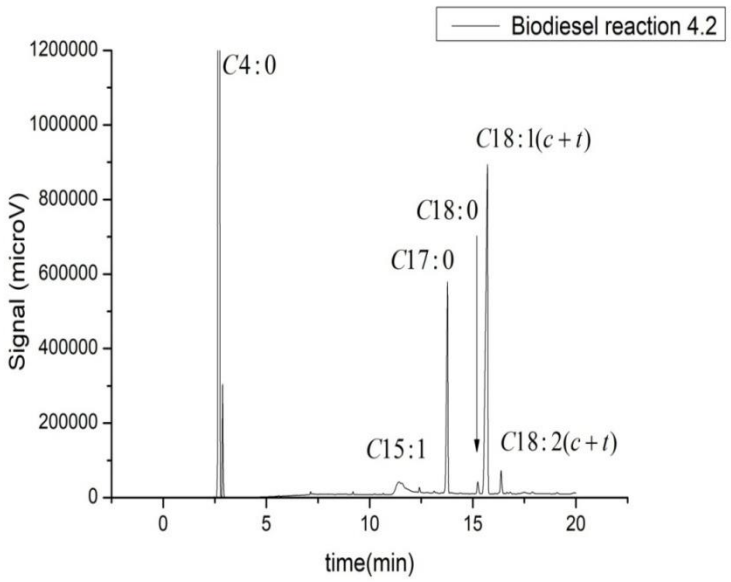


Figure 20. Chromatogram obtained after the derivatization of FAME for biodiesel reaction 4.2.

From the GC-FID analysis for reaction 4.2 the main fatty acids constituting the analyzed are 1.3% of cis-10-Pentadecanoic acid methyl ester C15:1, 0.1% of stearic acid methyl ester C18:0, 47.8 % of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 2.5% of Linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). Corresponding to the internal standard, biodiesel reaction 1.1 makes up a total percentage of FAMEs of 51.76%. Table 16 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 4.2.

Table 16. FAME content for each of the identified esters (ID) for reaction 4.2.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	1.3%
Stearic acid methyl ester	C18:0	0.1%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	47.8%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	2.5%

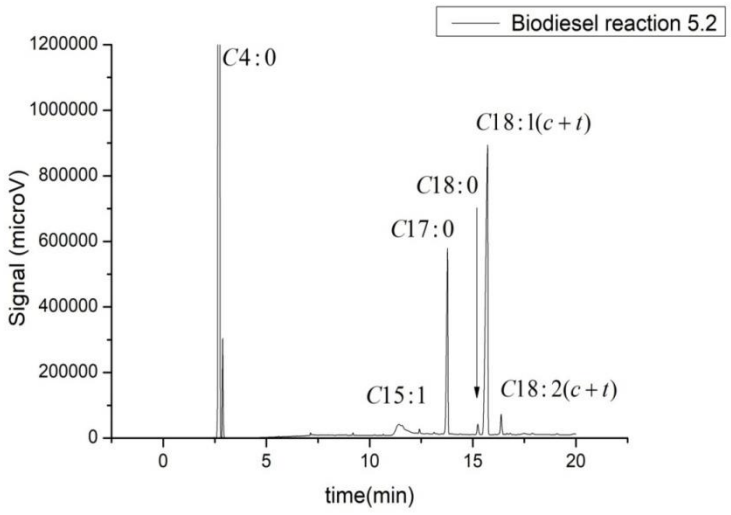


Figure 21. Chromatogram obtained after the derivatization of FAME for biodiesel reaction 5.2.

From the GC-FID analysis for reaction 5.2 the main fatty acids constituting the analyzed are 1.7% of cis-10-Pentadecanoic acid methyl ester C15:1 ,0.5% of stearic acid methyl ester C18:0, 56.2% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 0.2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). Corresponding to the internal standard, biodiesel reaction 5.2 makes up a total percentage of FAMEs of 58.76%. Table 17 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 5.2.

Table 17. FAME content for each of the identified esters (ID) for reaction 5.2.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	1.7%
Stearic acid methyl ester	C18:0	0.5%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	56.2%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.2%

***GC results for the 20% load of catalyst.

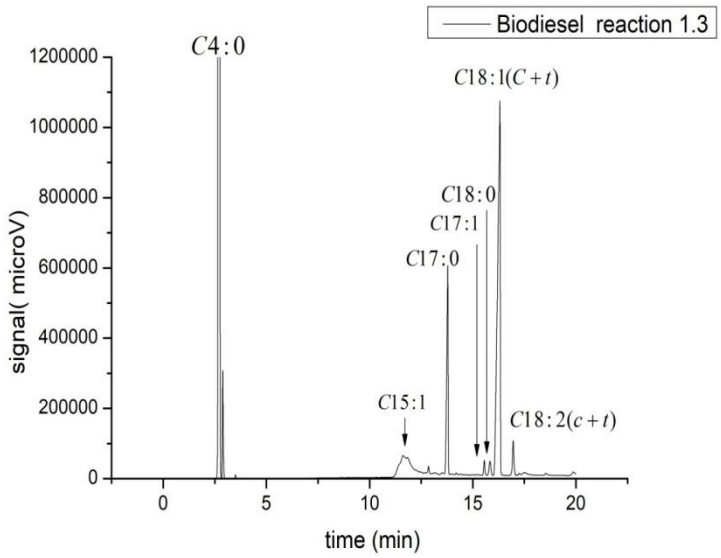


Figure 22. Chromatogram obtained after the derivatization of FAME for biodiesel reaction 1.3.

From the GC-FID analysis for reaction 1.3 the main fatty acids constituting the analyzed are 9% of cis-10-Pentadecanoic acid methyl ester C15:1, 1% of cis-10-Heptadecanoic acid methyl ester C17:1, 1% of stearic acid methyl ester C18:0, 66% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). Corresponding to the internal standard, biodiesel reaction 1.3 makes up a total percentage of FAMEs of 78.26%. Table 18 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 1.3.

Table 18. FAME content for each of the identified esters (ID) for reaction 1.3.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	9%
cis-10-Heptadecanoic acid methyl ester	C17:1	1%
Stearic acid methyl ester	C18:0	1%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	66%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	2%

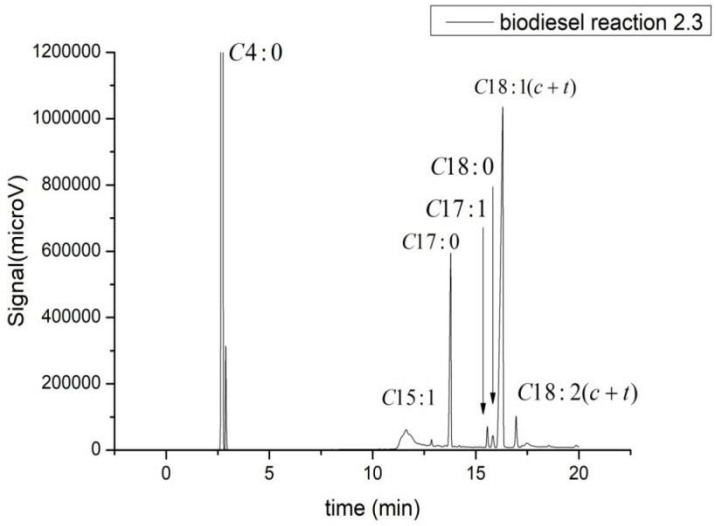


Figure 23. Chromatogram obtained after the derivatization of FAME for biodiesel reaction 2.3.

From the GC-FID analysis for reaction 2.3 the main fatty acids constituting the analyzed are 15% of cis-10-Pentadecanoic acid methyl ester C15:1, 0.4% of cis-10-Heptadecanoic acid methyl ester C17:1, 2% of stearic acid methyl ester C18:0, 64% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). Corresponding to the internal standard, biodiesel reaction 2.3 makes up a total percentage of FAMEs of 92.98%. Table 19 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 2.3.

Table 19. FAME content for each of the identified esters (ID) for reaction 2.3.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	15%
cis-10-Heptadecanoic acid methyl ester	C17:1	0.4%
Stearic acid methyl ester	C18:0	2%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	64%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	2%

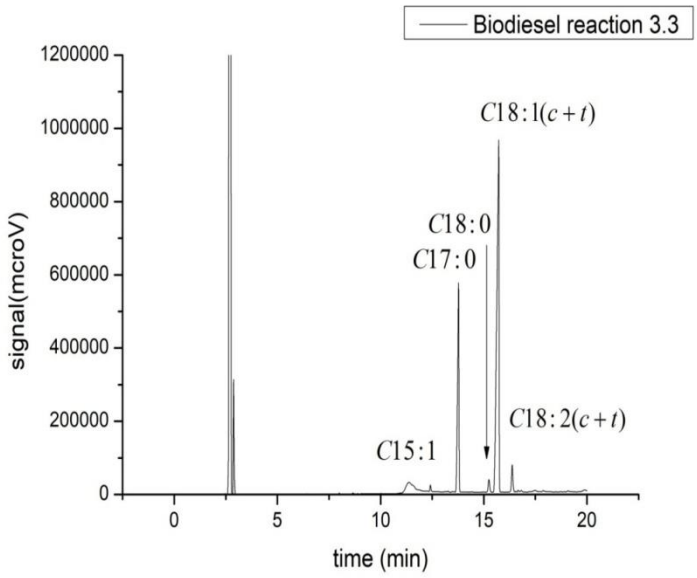


Figure 24. Chromatogram obtained after the derivatization of FAME for biodiesel reaction 3.3.

From the GC-FID analysis for reaction 3.3 the main fatty acids constituting the analyzed are 1% of cis-10-Pentadecanoic acid methyl ester C15:1, 0.1% of stearic acid methyl ester C18:0, 52.5% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 0.2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). Corresponding to the internal standard, biodiesel reaction 3.3 makes up a total percentage of FAMEs of 53.46%. Table 20 presents the qualitative and quantitative characterization of each fatty acid methyl ester in biodiesel reaction 3.3.

Table 20. FAME content for each of the identified esters (ID) for reaction 3.3.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	1%
Stearic acid methyl ester	C18:0	0.1%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	52.2%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.2%

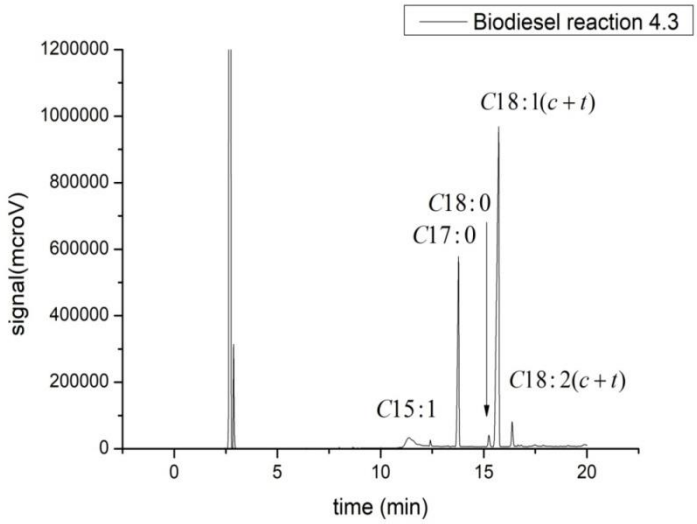


Figure 25. Chromatogram obtained after the derivatization of FAME for biodiesel reaction 4.3.

From the GC-FID analysis for reaction 4.3the main fatty acids constituting the analyzed are 1% ofcis-10-pentadecanoic acid methyl ester C15:1, 0.1% of stearic acid methyl ester C18:0, 58.1% of oleic acid methyl ester, elaidic acid methyl ester C18:1(c+t), 0.2% of linoleic acid methyl ester, linolelaidic acid methyl ester C18:2(c+t). In relation to the internal standard, the total percentage of FAMEs is 59.39%. Table 21 presents the qualitative and quantitative characterization of each fatty acid methyl ester for biodiesel reaction 4.3.

Table 21. FAME content for each of the identified esters (ID) for reaction 4.3.

Compound name	Compound ID	FAME (%)
cis-10-Pentadecanoic acid methyl ester	C15:1	1%
Stearic acid methyl ester	C18:0	0.1%
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	58.1%
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	0.2%

The evolution of the esterification reaction was quantified in terms of the content of fatty acid methyl esters (FAMEs) produced, and GC-FID analyses of the obtained biodiesel samples were performed. The biodiesel samples for different reaction amount of catalyst 10%, 15% and 20%.

The optimal value found for the conversion in term of FAME's content was 82.98%, obtained using 20 % of ionic liquid, molar ratio oleic acid/methanol 1:10, 4 hours of reaction and 65°C of temperature.

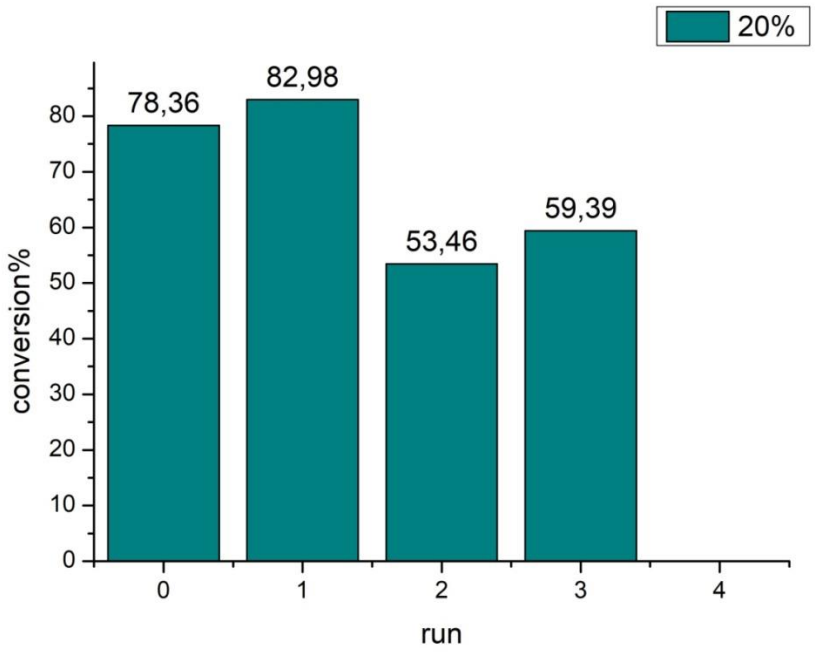


Figure 26. Reaction conversions dependency from 20% amount of catalyst and 4 runs.

The optimal values found for the conversion was 73.07%, were obtained using 10 % of ionic liquid, molar ratio oleic acid/methanol 1:10, 4 hours of reaction and temperature of 65 °C.

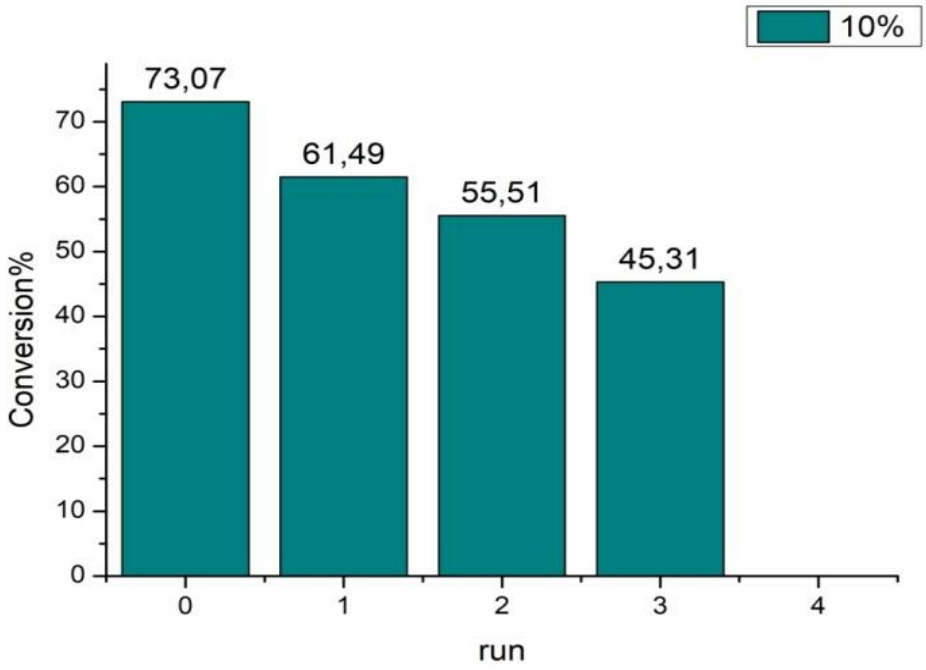


Figure 27. Reaction conversions dependency from 10% amount of catalyst and 4 runs.

The optimal values found for the conversion was 91.26%, were obtained using 15 % of ionic liquid, molar ratio oleic acid/methanol 1:10, 4 hours of reaction and temperature of 65 °C.

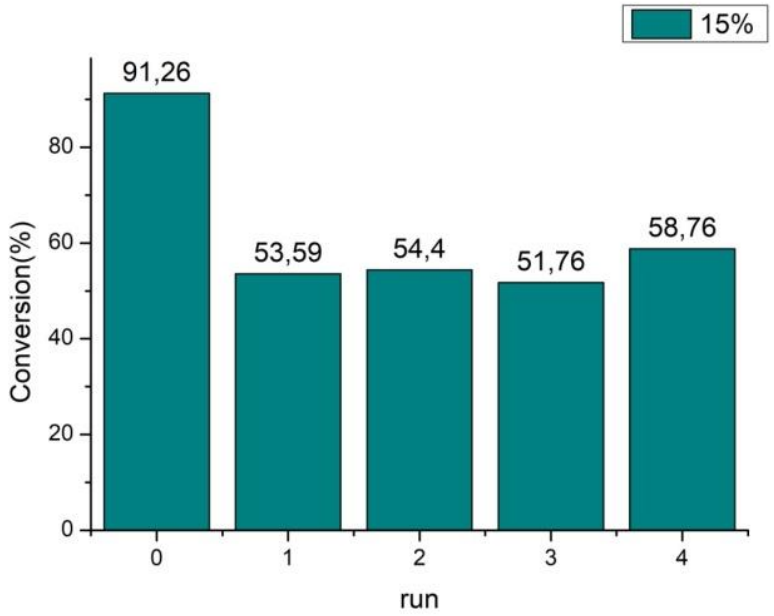


Figure 28. Reaction conversions dependency from 15% amount of catalyst and 5 runs.

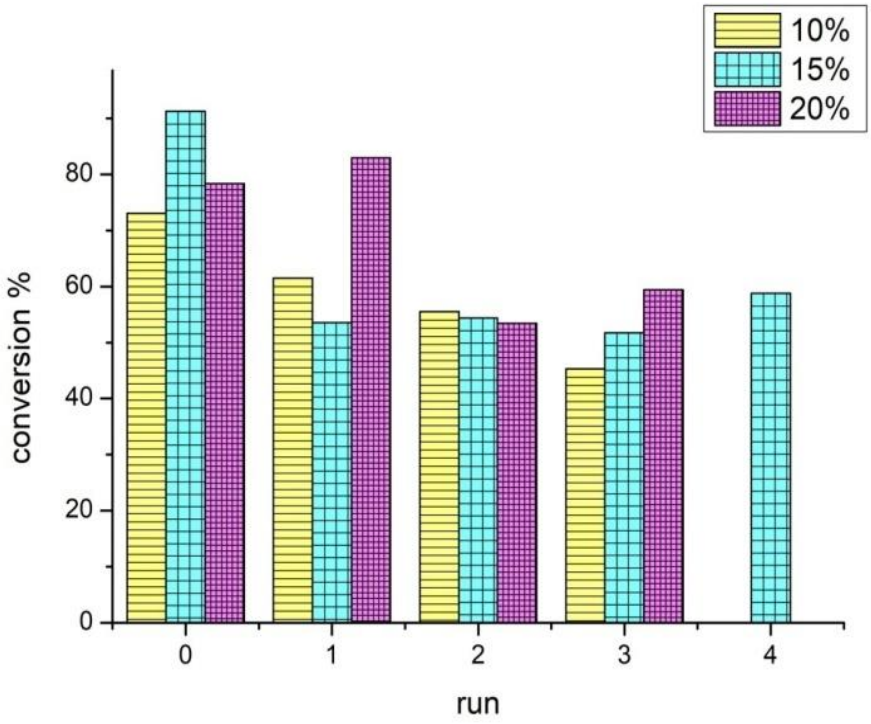


Figure 29. Effect of the amount of catalyst on the reaction conversions.

Analyzing the experimental results, it is verified that the conversion has the highest value, of conversion in term of FAMEs, of 59.39% at the fourth cycle of reusing the catalyst for a catalyst amount of 20%. However, the conversion obtained for the catalyst amount 15% is 58.78 % after 5 runs is very similar to that obtained for 20 % of amount of catalyst of reaction and the conversion with 10% after the fourth cycle is 45.31%, Thus it is considered that an increase in the amount of catalyst does not significantly change the conversion of the reaction. It is known that a significant migration of oleic acid to the aqueous phase during the phase separation process is possible.

5.5. FTIR Analysis

The FTIR analysis was performed in order to verify the efficiency of the ionic liquid recovery. For a better understanding of the analysis performed and identification of each compound in the mixture, it was first carried out the study of the spectra of the existing compounds in the initial mixture, ionic liquid (IL) methanol (MeOH) and oleic acid (OA). To better understand and interpret the spectra, it is important to know the characteristic regions of the spectrum associated with the functional groups of the studied compounds. The absorption in the infrared

band (IR) of organic molecules in certain areas of the spectrum is due to different interactions, specific to the functional groups present. These functional groups thus present characteristic absorptions in different spectrum zones (defined in terms of wave numbers, cm^{-1} due to vibrational interaction modes. The intensity of the bands can be presented in absorbance (A) or transmittance (T), being the transmittance defined as the existing ratio between the transmitted power and the incident power of the sample. The absorbance is the logarithm (log10) of the inverse of the transmittance. (Silverstein *et al***,** 2005)

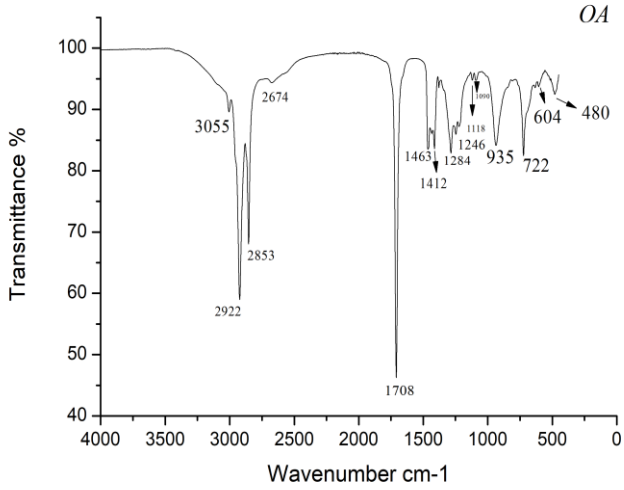


Figure 30. FTIR spectra of pure oleic acid (liquid).

The FT-IR spectra of the pure oleic acid liquid presents the following characteristic bands: it is displayed a wide and intense band due to O-H bond between at 2674 cm^{-1} and 3055 cm^{-1}, centered at 3055 cm^{-1}. The bands corresponding to the (-CH_2-) asymmetric and the symmetric stretching at 2922 cm^{-1} and 2853 cm^{-1} were arranged in the elongation of O-H bond . The C=O stretching band at 1708 cm^{-1} has been ascribed to a dimeric oleic acid. The band at 1284 cm^{-1} is attributed to the C-O elongation and the intense band at 1412 cm^{-1} is characteristic of the angular deformation of C-O-H bond. The band at 935 cm^{-1} results from an angular deformation outside the plan of O-H bond, and is characteristic of the dimeric oleic acid (see Figure 30). (Labidi *et al.*, 2007)

Figure 31 displays the FT-IR for the methanol. The most characteristics IR absorption bands for alcohols are in the range of 3309–2943 cm^{-1}, related to the stretching vibration of the -OH Therefore, the broad band centered at 3309 cm^{-1} is assigned to the OH stretching and the strong band at 1022 cm^{-1} to the C-O bond. The bands at 2943 and 2520 cm^{-1} are related to aliphatic

CH stretching. The band at 1448 cm^{-1} is related to the symmetric CH_3 umbrella deformation, which is overlapped by the out of plane C-OH deformation at 1416 cm^{-1}. The out-of-plane C-OH deformation gives rises to a second broad band, which is identified as the one at 631 cm^{-1}. (Silverstein *et al.*, 2005)

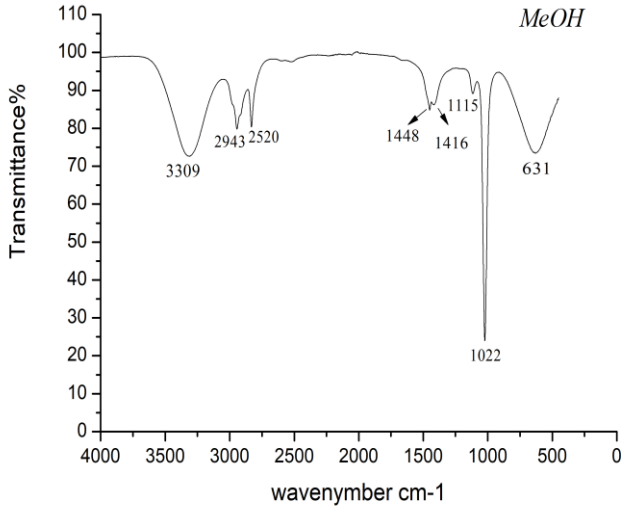


Figure 31. FTIR spectra of pure methanol.

The FT-IR analysis of the ionic liquid, [HMIM]HSO_4 which structure is showed in Figure 32 for this heterocyclic compounds with two double bonds in a five-membered ring shows three ring vibrations near 1586, 1552 and 1454 cm^{-1}. The CH stretch for heteroaromatic rings containing nitrogen falls in the region 3148–3078 cm^{-1}. Therefore, the bonds at 1586, 1552 and 1454 cm^{-1} are related to the ring in the imidazolium cation and the band at 3148cm^{-1} can be ascribed to the stretching vibration of the CH bonds in the cation. Most of five-membered rings containing a CH=CH unsubstituted group have strong hydrogen wag absorption in the region 900–700 cm^{-1} and therefore the bands at 838 and 756 cm^{-1} can be associated with this vibration. The band at 2967 cm^{-1} is attributed to the out-of-phase CH_3 stretch and the band at 2872 cm^{-1} to the in-phase CH_3 stretch. The group HSO_4^{-1} has two absorption bands: one from 1281–1156 cm^{-1} related to the asymmetric SO_3 stretch and at 1023 cm^{-1} related to the symmetric SO_3 stretch. Consequently bands 11556 and 1023 cm^{-1} can be ascribed to the anion. (Silverstein *et al.*, 2005)

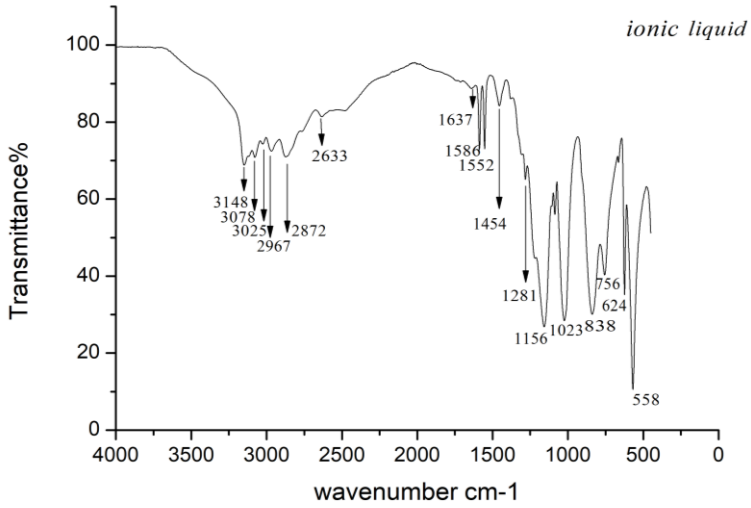


Figure 32. FTIR spectra of pure [HMIM]HSO_4.

5.6 Recovery of ionic liquid

The effect of the recovery steps in the quality of the ionic liquid was studied by Fourier Transform Infra-Red (FTIR) spectroscopy. Table 22 displays the % of the recovered IL for each cycle after washing with water using a 1:3 mass ratio, and drying in the oven.

****Recovery by washing**

Liang *et al.*, 2019 tested the recovery process of the basic ionic liquid chloraluminate/triethylammonium chloride [ETNH]Cl-$AlCl_3$ by a washing method using ethyl acetate as solvent, to remove the organic esters.(Liang et *al*., 2009)

Thus, it was proceeded to the test of the washing process for the recovery of the ionic liquid through a study with distillated water, because the ionic liquid tested shows hydrophilic characteristics, which allows its total miscibility in water. The test was carried out applying a mass ratio of 3:1 solvent relative to the sample weight, followed by a decanting step for visualization of the formation of two phases. In fact, it was observed the separation of the two phases admitting that the ionic liquid was collected in the denser lower phase and the remainder of the compounds present in the mixture were essentially in the less dense upper phase. Therefore, it was possible to recover the ionic liquid from the corresponding sample obtained from the reaction.

Table 22. % mass of recovered ionic liquid and drying conditions.

1	Assay	Drying time (hr) after washing with water	Recovery of IL	Recovery compared to the previous cycle
0	**1.1**	5h in the oven	74%	74%
1	**2.1**	22 h in the oven	62%	62%
2	**3.1**	15 h in the oven	60%	44%
3	**4.1**	24 h in the oven	51%	31%
0	**1.2**	34 h in vacuum oven 60°C	91%	91%
1	**2.2**	24h in vacuum oven 60°C	75%	75%
2	**3.2**	24 h in vacuum oven 70°C	78%	65%
3	**4.2**	24 h in vacuum oven 70°C	69%	59%
4	**5.2**	24 h in vacuum oven 70°C	79%	69%
0	**1.3**	24 h in vacuum oven 70°C	83%	91%
1	**2.3**	24 h in vacuum oven 70°C	98%	75%
2	**3.3**	24 h in vacuum oven 70°C	94%	78%
3	**4.3**	24 h in vacuum oven 70°C	93%	69%

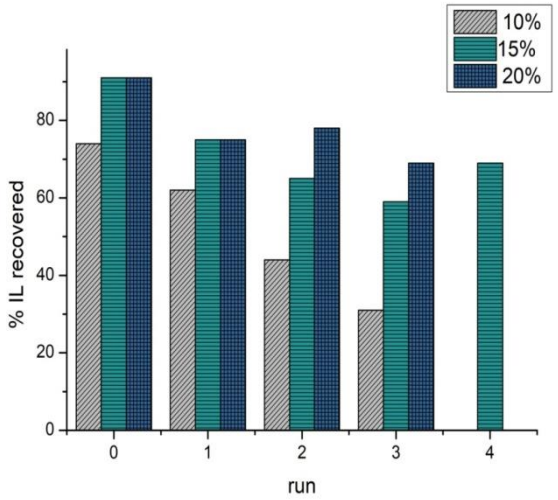


Figure 33. % mass of recovered ionic liquid.

The reaction yield was found to be 74% to 10% IL, 91% to 15% IL and 91% to 20% IL. These yields decreased to 44% (10% IL) with 4 cycles of recycling, 69% (15% IL) with 5 cycles of recycling and 69% (20% IL) with 5 cycles of recycling.

Tadevosyan, 2017, tried the esterification reaction of oleic acid with [BMIM] [HSO_4]. At second part of the work, the recovery of [BMIM] [HSO_4] was studied and several esterification reactions of oleic acid were carried out using a quantity of catalyst of 10 wt%, 15 wt% and 20 wt% relative to the mass of oleic acid. The experimental conditions were as follows: reaction time 6 hours, oleic acid / methanol molar ratio 1:10 and temperature 90 °C. The reaction yield was found to be 73.07% to 10% IL, 91.26% to 15% IL and 82.39% to 20% IL. These yields decreased to 45.31% (10% IL) with 4 cycles of recycling, 45.31% (15% IL) with 5 cycles of recycling and 59.39% (20% IL) with 4 cycles of recycling.

The spectrum of original IL and the ILs recovered after the final esterification reaction, for each amount of catalyst displayed in Figures 34, 35 and 36.

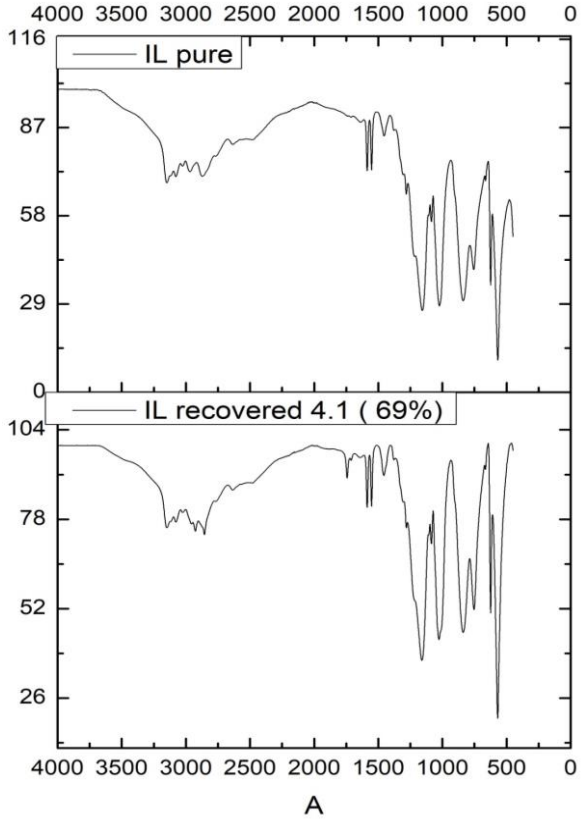


Figure 34. FTIR spectrum obtained for original IL 10% (REC4.1) with 69% of correlation.

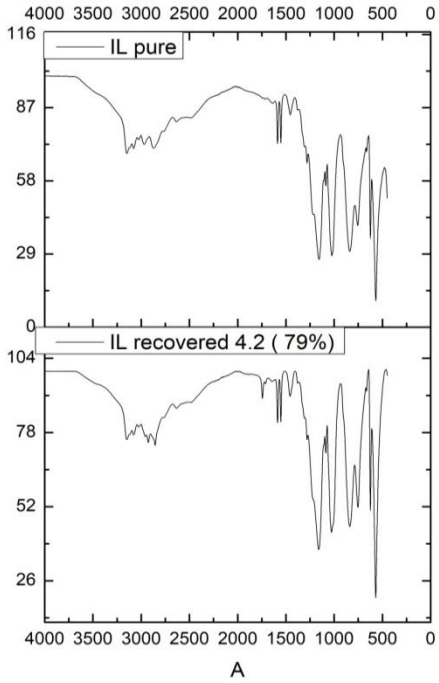


Figure 35. FTIR spectrum obtained for original IL 15% (REC5.1) with 79% of correlation.

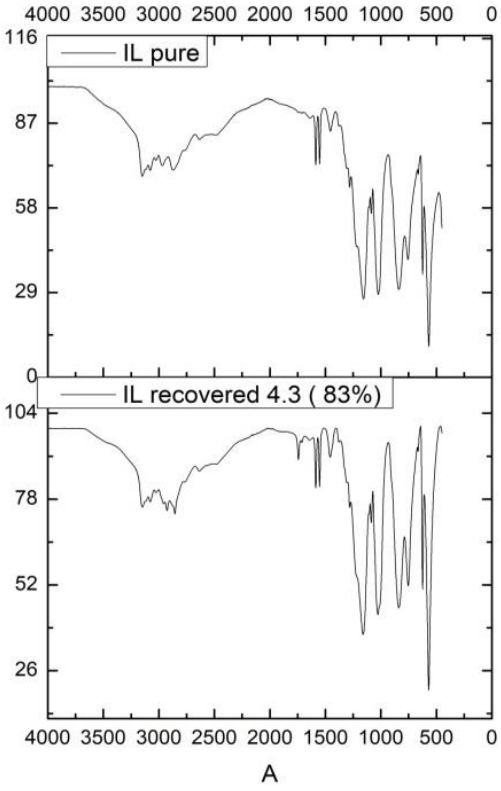


Figure 36. FTIR spectrum obtained for original IL 20% (REC4.3) with 83% of correlation.

5.7. Acid value measurement

To evaluate the performance the ionic liquid 1-methylimidazolium hydrogen sulfate [HMIM] [HSO_4] in the production of biodiesel through the esterification reaction of oleic acid in the presence of methanol we have measured the acidity of the organic phase before drying using equation 2. Table 23 shows the conversion value in term of acidity for the reactions with the three different contents of IL 10%, 15%, 20%.

Table 23. Dependency of conversion in term of AV for 10% IL, 15% IL, 20% IL.

Cycle	Assay	Conversion X (%)
1	2.1 (10% IL)	75,01
2	3.1 (10% IL)	72,34
3	4.1 (10% IL)	71,36
0	1.2 (15% IL)	82,36
1	2.2 (15% IL)	77,84
2	3.2 (15% IL)	77,00
3	4.2 (15% IL)	75,79
4	5.2 (15% IL)	70,88
0	1.3 (20% IL)	77,35
1	2.3 (20% IL)	75,89
2	3.3 (20% IL)	75,65
3	4.3 (20% IL)	75,27

The reaction conversion in terms of acidity calculated by analyzing the organic phase was found to be 75.01% to 10% IL, 82.36% to 15% IL and 77.35% to 20% IL. These conversion value decreased to 71.36% (10% IL) with 4 cycles of recycling, 70.88% (15% IL) with 5 cycles of recycling and 75.27% (20% IL) with 4 cycles of recycling. The highest acidity value was with 20% of IL it was 82.36 % to decrease to 70.88% after 5 runs.

6. Conclusions

This work sought to determine the capacity of ionic liquid [HMIM][HSO_4] as a catalyst in the esterification reaction of oleic acid with methanol. The condition of the work was reaction time of 4 hours, a molar ratio oleic acid 1:10 methanol, for a temperature of 65 °C, with 3 different catalyst amounts 10%, 15% and 20 %.

The reaction yield was found to be 74% to 10% IL, 91% to 15% IL and 91% to 20% IL. These yields decreased to 44% (10% IL) with 4 cycles of recycling, 69% (15% IL) with 5 cycles of recycling and 69% (20% IL) with 4 cycles of recycling.

In this study, performing the calculation of the conversion applying equation 4, the highest value of conversion in terms of FAMEs was 59.39% at the fourth cycle of reusing the catalyst for a catalyst amount 20%. The highest acidity value was with 20% of IL which decreased from 82.36 % to 70.88% after 5 runs.

In the case of a hydrophilic ionic liquid, the recovery process was carried out using water in the washing of IL .After this process, it was necessary to ensure that all the water used was removed and a drying process was performed in a vacuum oven at 70°C, and at 60°C. The results obtained showed that washing using water as a solvent is an effective method recovering samples with 69% correlation of the FTIR spectrum in relation to the original IL. For reactions with 10% IL, 79% correlation with 15% amount of catalyst, 83% correlation with a 20% amount of catalyst

In conclusion, the use of ionic liquids as catalysts in the production of biodiesel has several advantages. The ionic liquid as a catalyst used in the present study presented good results of conversion and ease of recovery. The ionic liquid studied showed very similar results for amounts of catalyst with 15% and 20% but the best one was get it with 20% of IL. The recovery of this ionic liquid was performed by using water as a solvent. This fact is likely to reduce the costs associated with the application of this ionic liquid as a catalyst in biodiesel conversion processes.

7. Future works

In order to be able to draw a conclusion on the applicability of the ionic liquid [HMIM]HSO_4 in the production of biodiesel it will be necessary to carry out further studies using the mentioned ionic liquid. Some suggestions for future work are:

(i) Study of the variables, reaction time, different molar ratio methanol/oleic acid and different temperature in order to determine the optimum conditions of these parameters in the reaction.

(ii) Study of the application of HMIM]HSO_4 as ionic liquid in the triglyceride transesterification reaction using raw materials with high acidity such as waste cooking oil

(iii) Develop the recovery of ionic liquid HMIM]HSO_4 by washing with other suitable solvents.

(iv) Assess the maximum number of recovery cycles that the ionic liquid can perform without significant loss of reaction yield.

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