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Biodiesel Production through Ionic Liquid Catalysed Esterification

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Abstract

Biodiesel is an alternative fuel diesel that can be produced from vegetable oils and animal fats. There is a recent growing interest in the development of alternative technologies to the oil economy, based on renewable energy sources. A possible solution is a biofuel usable in compression-ignition engines, produced from biomass rich in fats and oils. A wide range of raw materials can be used in the production of biodiesel. Nevertheless, the use of sources that do not compete with the food market like waste cooking oils, which usually feature high levels of free fatty acids (FFA's), can put problems in the process of production of biodiesel through alkaline transesterification. These problems are partially overcome by the use of catalysts, such as ionic liquids (IL's) that also promote reactions of esterification of FFA's to biodiesel. Thus, the objective of this work consists in the study of the influence of IL's application in the catalysis of: esterification reactions of organic acids to the corresponding methyl esters.

In the first part of the work the influence, as catalysts, of several ionic liquids in the esterification reaction of oleic acid was analyzed. The experimental conditions were as follows: reaction time 6 hours, oleic acid / methanol molar ratio = 1/10 and temperature 90 ° C. The ionic liquids evaluated were as follows: 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]), 1-butyl-3-methylimidazolium methanesulfonate ([BMIM][CH_3SO_3]), 1-butyl-3-methylimidazolium methylsulfate ([BMIM][CH_3SO_4]), 1-metylimidazolium hydrogen sulfate ([MIM][HSO_4]) and tributylmethylammonium methylsulfate. The values obtained for the conversion of the oleic acid esterification reaction showed that the ionic liquid [BMIM] [HSO_4] would be one of the most promising catalysts.

In a second part of the work, the recovery of LI [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 76.6% to 10% IL, 83.3% to 15% IL and 84.8% to 20% IL. These yields decreased to 58.2% (10% IL) with 4 cycles of recycling, 75.2% (15% IL) with 5 cycles of recycling and 77.1% (20% IL) with 5 cycles of recycling. The results obtained confirm that it is possible to reuse this IL in successive reactions of esterification without great loss of yield and with this to significantly reduce the costs associated with the purchase of these compounds that are quite expensive.

Keywords: Biodiesel, Esterification, Ionic Liquids, Recovery

Resumo

O biodiesel é um combustível alternativo que pode ser produzido a partir de óleos vegetais e de gorduras animais. Atualmente existe um crescente interesse no desenvolvimento de tecnologias alternativas à economia do petróleo baseadas em fontes de energia renováveis. Uma possível solução é a utilização de um biocombustível em motores de compressão-ignição, produzido a partir de biomassa rica em óleos e gorduras. Para a produção de biodiesel pode ser usada uma ampla gama de matérias-primas. No entanto, o uso de fontes que não competem com o mercado alimentar, como por exemplo os óleos alimentares usados, que geralmente têm um elevado nível de ácidos gordos livres (AGL´s), pode trazer problemas ao processo de produção de biodiesel através da transesterificação alcalina. Estes problemas são parcialmente ultrapassados usando catalisadores, tais como os líquidos iónicos (LI´s), que também promovem as reações de esterificação dos AGL´s a biodiesel.

Assim, o objetivo desta dissertação de mestrado consistiu no estudo da aplicação de líquidos iónicos como catalisadores nas reações de esterificação de ácidos orgânicos aos correspondentes ésteres metílicos.

Na primeira parte do trabalho analisou-se a influência, como catalisadores, de diversos líquidos iónicos na reação de esterificação do ácido oleico. Os líquidos iónicos avaliados foram os seguintes: 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]), 1-butyl-3-methylimidazolium methanesulfonate ([BMIM][CH_3SO_3]), 1-butyl-3-methylimidazolium methylsulfate ([BMIM][CH_3SO_4]), 1-metylimidazolium hydrogen sulfate ([MIM][HSO_4]) and tributylmethylammonium methylsulfate. Os valores obtidos para a conversão da reação de esterificação do ácido oleico mostraram que o líquido iónico [BMIM][HSO_4] seria um dos mais promissores como catalisador.

Numa segunda parte do trabalho procedeu-se ao estudo da recuperação do LI [BMIM][HSO_4], tendo-se realizado diversas reações de esterificação do ácido oleico usando uma quantidade de catalisador de 10%, 15% e 20% (m/m) relativamente à massa de ácido oleico. As condições experimentais foram as seguintes: tempo de reação 6 horas, razão molar ácido oleico/metanol = 1/10 e temperatura 90 °C. Verificou-se que o rendimento da reação foi de 76,6 % para 10% de LI, 83,3% para 15% de LI e 84,8% para 20% de LI. Estes rendimentos diminuíram para 58,2% (10% de LI) com 4 atapas de reciclagem, 75,2% (15% de LI) com 5 etapas de reciclagem e 77,1% (20% de LI) com 5 etapas de reciclagem. Os resultados obtidos permitem confirmar que é possível reutilizar este LI em reações sucessivas de esterificação sem grande perda de rendimento e com isso diminuir significativamente os custos associados à compra destes compostos que são bastante caros.

Palavras-chave: Biodiesel, Esterificação, Líquidos Iónicos, Reutilização

Համառոտագիր

Կենսադիզելն այլընտրանքային դիզելային վառելիք է, որն ստացվում է բուսական յուղերից և կենդանական ճարպերից: Վերջին շրջանում աճում է հետաքրքրությունն այլընտրանքային տեխնոլոգիաների՝ նավթային տնտեսության, հիմականում վերականգնվող էներգիայի աղբյուրների նկատմամբ: Հնարավոր լուծում է ներքին այրման շարժիչներում կենսավառելիքի օգտագործումը, որն արտադրված է ճարպերով և յուղերով հարուստ կենսազանգվածից: Կենսադիզելի արտադրության մեջ հնարավոր է օգտագործել հումքի լայն ընտրանի: Օգտագործվող հումքի աղբյուրները չեն մասնակցում պարենային շուկայի մրցակցությանը: Այդպիսիք են՝ խոհանոցային թափոններ հանդիսացող յուղերը, որոնք հիմնականում բնորոշվում են խնդրահարույց ազատ ճարպային թթուների (ԱՃԹ) մեծ պարունակությամբ: Այս խնդիրը մասամբ հաղթահարվել է՝ օգտագործելով կատալիզատորներ, ինչպիսիք են իոնային հեղուկները (ԻՀ), որոնք նույնպես նպաստում են կենսադիզելում ԱՃԹ-ի եթերացմանը: Այսպիսով, այս աշխատանքի նպատակն է ուսումնասիրել իոնային հեղուկ կատալիզատորների ազդեցությունը համապատասխան մեթիլեթերների հետ օրգանական թթուների եթերացման ռեակցիաներում:

Աշխատանքի առաջին մասում հետազոտվել է մի քանի իոնային հեղուկների ազդեցությունն օլեինաթթվի եթերացման ռեակցիայում: Փորձի պայմանները հետևյալն են. ռեակցիայի ժամանակը ՝ 6 ժամ, օլեինաթթու / մեթանոլ մոլային հարաբերակցությունը՝ 1/10, ջերմաստիճանը 90°C: Հետազոտվող իոնային հեղուկները հետևյալն են. 1-բութիլ-3-մեթիլիմիդազոլիումի հիդրոսուլֆատ ([BMIM][HSO_4]), 1-բութիլ-3-մեթիլիմիդազոլիումի մեթանսուլֆոնատ ([BMIM][CH_3SO_3]), 1-բութիլ-3-մեթիլիմիդազոլիումի մեթիլսուլֆատ ([BMIM][CH_3SO_4]), 1-մեթիլիմիդազոլիումի հիդրոսուլֆատ ([MIM][HSO_4]) և տրիբութիլմեթիլամոնիումի մեթիլսուլֆատ: Օլեինաթթվի եթերացման ռեակցիայի արդյունքները ցույց տվեցին, որ [BMIM][HSO_4] իոնային հեղուկն ամենախոստումալից կատալիզատորներից մեկն է:

Աշխատանքի երկրորդ մասում ուսումնասիրվել են [BMIM][HSO_4] իոնային հեղուկի վերականգնումը և օլեինաթթվի եթերացման մի քանի ռեակցիաներ, որոնցում օգտագործված կատալիզատորի զանգվածը եղել է օլեինաթթվի զանգվածի 10%, 15%, 20%-ը: Փորձի պայմանները հետևյալն են. ռեակցիայի ժամանակը ` 6 ժամ, օլեինաթթու / մեթանոլ մոլային հարաբերակցությունը` 1/10, ջերմաստիճանը 90°C: Ռեակցիայի ելքը կազմել է 76.6% ԻՀ-ի 10%-ի դեպքում, 83.3% ` ԻՀ-ի 15%-ի դեպքում և 84.8%` ԻՀ-ի 20%-ի դեպքում: Այս ելքերը նվազել են մինչև 58.2% (10% ԻՀ)` վերամշակման 4 ցիկլից հետո, 75.2% (15% ԻՀ)` վերամշակման 5 ցիկլից հետո, 77.1% (20% ԻՀ)` վերամշակման 5 ցիկլից հետո: Ստացված արդյունքները հաստատում են, որ հնարավոր է այս ԻՀ-ի վերաօգտագործումը եթերացման հաջորդական ռեակցիաներում` առանց ելքի մեծ կորստի, և զգալիորեն նվազեցնել այդ, բավականին թանկ, միացությունների գնման հետ կապված ծախսերը:

Առանցքային բառեր. կենսադիզել, եթերացում, իոնային հեղուկ, վերամշակում:

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List of abbreviations

FFA	Free Fatty Acids
IL	Ionic Liquid
FAME	Fatty Acidy Methyl Ester
HVO	Hydro treated Vegetable Oil
BTL	Biomass to Liquid Fuel
DES	Deep Eutectic Solvent
AC	Activated Carbon
FID	Flame Ionization Detector
GC	Gas Chromatography
wt	Weight
t	Time
T	Temperature
UV	Ultra-Violet
$SCCO_2$	Supercritical Carbon Dioxide
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared
ART	Attenuated Total Reflection

List with the name materials

NO_X	Nitrogen Oxides
NaOH	Sodium hydroxide
BF_4^-	Tetrafluoroborate
PF_6^-	Hexafluorophosphate
$CH_3CO_2^-$	Acetate
$CF_3CO_2^-$	Trifluoroacetate
NO_3^-	Nitrate
$[Al_2Cl_7]^-$	heptachlorodialuminate
BASIL	Biphasic Acid Scavenging Using Ionic Liquids
[Hnmm] OH	1-butyl-3-methyl morpholine hydroxide
MeOH	Methanol
[C2MIM][TfO]	1-butyl-3-methylimidazolium trifluoromethanesulfanate
[C4MIM] $[NTf_2]$	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[C18MIM][NTf_2]$	1-octadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[C16MIM][NTf_2]$),	1-Hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[BMI][PF_6]$)	1-n-butyl-3-methylimidazolium hexafluorophosphate
$[BMI][BF_4]$	1-n-butyl-3-methylimidazolium tetrafluoroborate
$[BMIM][FeC_{l4}]$	1-butyl-3-methylimidazolium tetrachloroferrate
$[HMIM]HSO_4$	1-hexyl-3-Methylimidazolium Hydrogen Sulfate
SiO_2	Silica

Al_2O_3	Alumina
TiO_2	Titanium dioxide
$[BMIMHSO_4]$	1-Butyl-3-Methylimidazolium Hydrogen Sulfate
$[PSPy][HSO_4]$	N-propane-sulfonic acid pyridinium hydrogen sulfate
$[NMP][HSO_4]$	N-methyl-2-pyrrolidonium hydrogensulfate
$[(CH_2)_4SO_3HMIM]\ [CF_3SO_3]$	1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate
$[(CH_2)_4SO_3HMIM]\ [HSO_4]$	1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate
KOH	Potassium hydroxide
HCl	Hydrochloric acid
He	Helium
H_2SO_4	Sulfuric acid
$[BMIM][MeSO_4]$	1-Butyl-3-methylimidazolium methyl sulfate
$[MIM][HSO_4]$	1-Methylimidazolium hydrogen sulfate

1 Introduction

Over the last three decades, the realisation of the limited petrochemical based energy resources has motivated an intense search for alternative transportation vehicles fuels. In this context, a possible solution is a biofuel usable in compression ignition engines (or diesel engines), produced from biomass rich in fats and oils. Thus, a wide range of raw materials can be used in the production of biodiesel. However, the use of sources that do not compete with the food market, like waste cooking oils, which usually feature high levels of free fatty acids (FFA's), can add problems to the classic process of biodiesel production through alkaline transesterification. These problems can be partially overcome by the use of catalysts, such as ionic liquids (IL's) that promote also the reactions of esterification of FFA's in biodiesel.

One of the attractive characteristics of biodiesel is that its use does not require any significant modifications to the diesel engine, so the engine does not have to be dedicated for biodiesel. However, similar to alcohol fuels, biodiesel has lower energy content and different physical properties than diesel fuels [*Tat et al., 2002*].

Biodiesel fuel has recently attracted increasing worldwide attention as a blending component or a direct replacement for diesel fuel in vehicle engines. For example, B5 used in Europe contains 5% of biodiesel (B100) and 95% of petro diesel. Biodiesel blends up to B20 can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment [*Ahmia et al., 2014*].

Biodiesel is a non-toxic, biodegradable and renewable fuel. It has significantly lower emissions than petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect and biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability [*Ahmia et. al., 2014*]. There is a wide range of raw materials suitable for the production of biodiesel. However, first generation edible oils are the main resources for world biodiesel production.

The main goal of this work consists in the study of the influence of IL's application in the catalysis of esterification and transesterification reactions which lead to the synthesis of fatty acid methyl esters (FAME) mixtures, which constitute the ester biodiesel products. The central focus is concerned with the study of IL recovery. For the recover and recycle of ILs the first used distillation. It is important to note that the interaction of ILs with water is mainly affected by the size of ILs, hydrophobicity and hydrogen bonding ability of both cations and anions, will determine the techniques used for recovery of ILs.

1.1 Background and Motivation

Alternative diesel fuel has attracted more attention in the last three decades. For this purpose, ester biodiesel has been studied as a source of bioenergy, which can potentially substitute petrochemical based diesel fuels.

Wide range of raw materials can be used in the production of biodiesel. It has the advantage of dramatically reduce sulphate, hydrocarbon and particulate matter emissions. It is nontoxic and does not contaminate water sources. Biodiesel is a fuel that can be made from pure or waste vegetable oils such as soy and rapeseed (canola) oils, and may be used in any diesel automotive engine in its pure form or blended with petroleum-based diesel, without the requirement of hardly any modification in the diesel engine, leading to a less-expensive, renewable and clean-burning fuel. However, the use of second generation non-edible sources, which do not compete with the food market like waste cooking oils and feature high levels of acidity, can induce difficulties in the operation of the classic process of production of biodiesel by alkaline transesterification. These problems can be overcome by the use of catalysts, such as ionic liquids (IL’s) that promote also the reactions of esterification of Free Fatty Acids (FFA’s) to biodiesel. In this work we will study the performance of imidazolium-based ionic liquids in the replacement of the classic homogeneous and heterogeneous, acid and alkaline catalysts generally used for the production of ester biodiesel. Imidazolium based ionic liquids are the most studied species for this type of applications, due to its inherent ionic patterns, low pressure and ability of self-organization in different states. This class of ionic liquids has been progressively used as green solvents in order to replace the volatile and relatively toxic organic solvents, in homogeneous and heterogeneous catalysis, materials science, nanomaterials, lithium ion batteries, and process separation technologies. Therefore, the main objective of this work consists in the study of the effect of the application of these IL's species in the catalysis of esterification reactions of organic acids to the corresponding methyl esters.

1.2 Structure of the report

Chapter 1 presents background and motivation. Chapter 2 of this thesis present an introduction to biodiesel as a renewable source, its properties and production processes. Chapter 3 is the literature review with information about ionic liquids and its types and properties. Chapter 4 gives a description of the experimental protocols developed and implemented and Chapter 5 presents the results and discussion of the work. Finally, in Chapter 6 the main conclusions and suggestions for future work are presented.

2 Biodiesel

2.1 Biodiesel as a renewable energy source

Biodiesel or ester based biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fat by transesterification with an alcohol (usually methanol). It is used as an additive to petrodiesel fuels, with different contents, promoting possible vehicle decreases greenhouse gas emissions up to 20%. It also can be used in its pure form as a renewable alternative fuel for diesel engines [*http://www.renewableenergyworld.com*]. Thus, biodiesel can be mixed in any proportion with petroleum diesel [*Tat et al., 2002*] and it does not contribute to a rise of the net concentration of carbon dioxide in the atmosphere, and leads to minimize the intensity of greenhouse effects [*Ahmia et al., 2014*].

2.2 Physicochemical properties

Biodiesel is a liquid biofuel, which colour ranges from golden to dark brown, depending on the production method and is slightly miscible with water. The main biodiesel physicochemical properties are given in Table 1.

Each of the most important physicochemical properties referred in Table 1 are explained in more detail below:

Kinematic Viscosity: It is defined as the resistance to flow of a fluid under gravity. It is a basic design specification for fuel injectors used in diesel engines. For biodiesel it is a quick and easy method for estimating the stage of completion of a batch synthesis reaction [*Biodiesel handling and use guide, 2016*].

Carbon residue: The carbon residue of a fuel is the tendency of carbon deposits to form under high temperature in an inert atmosphere. Using ordinary diesel fuel, the carbon residue is measured using a 10% distillation residue. Because B100 boils entirely at the high end of the diesel fuel range and in a very narrow temperature range, it is difficult to leave only a 10% residue when distilling biodiesel. So, for biodiesel carbon residue measurements, all biodiesel samples have to be used rather than the 10% distilled residue [*Biodiesel handling and use guide, 2016*].

Table 1. Biodiesel main properties [*Biodiesel handling and use guide, 2016*].

Fuel properties	**Biodiesel**
Kinematic viscosity at 40^0C, mm^2/s	4.0 to 6.0
Carbon, wt%	77
Total glycerol, wt%	0.240
Free glycerol, wt%	0.02
Sulphated ash, wt%	0.020
Flash point, ^{0}C	100-170
Boiling point, ^{0}C	315-350
Sulphur, wt%	0.0 to 0.0015
Pour point, ^{0}C	-5 to 10
Cloud point, ^{0}C	-3 to 15
Cetane number	47 to 60
Higher heating value (MJ/kg)	42.65
Lower heating value (MJ/kg)	33-42

Total Glycerol: Total glycerol is the sum of free and bonded glycerol [*Taimur, 2011*]**.**

Free Glycerol: Free glycerol is the glycerol present as molecular glycerol in the fuel. It results from incomplete separation of the ester and glycerol products after the transesterification reaction. This can be a result of imperfect water washing or other approaches that do not effectively separate the glycerol from the biodiesel [*Taimur, 2011*]**.**

Bonded glycerol: Is the glycerol portion of the mono-, di-, and triglyceride molecules. High values of total glycerin are indicators of incomplete esterification reactions and predictors of excessive carbon deposits in the engine**.**

Sulphated Ash: Sulphated ash is a residue remaining after a fuel sample has been carbonized. The residue is then treated with sulphuric acid and heated to a constant weight. This test controls the mineral ash residual when fuel is burned. For biodiesel, this test is an important indicator of the amount of residual metals in the fuel that came from the catalyst used in the esterification process [*Taimur, 2011*]**.**

Flash point: Flash point of a fuel is defined as the temperature at which it will ignite when exposed to flame or spark [*Ved et al., 2013*]. A minimum flash point for diesel fuel is required for fire safety. B100 flash point value must be at least 93°C to provide that all the excess alcohol introduced in the production process is removed from the final biodiesel product.

Sulphur: Biodiesel must have less than 15 ppm in sulphur content, in order to reduce sulphate and sulfuric acid pollutant emissions [*Biodiesel handling and use guide, 2016*].

Pour point: The temperature at which the fuel contains so many agglomerated crystals, that it is essentially a gel and will no longer flow. Distributors and blenders use pour point as an indicator of whether the fuel can be pumped; otherwise it would not be suitable for use without heating or other treatment procedures [*Biodiesel handling and use guide, 2016*].

Cloud point: It is the most frequently used indicator of low-temperature operability. Fuels are generally expected to operate at temperatures as low as their cloud point. The cloud point of B100 is typically higher than the cloud point of conventional diesel fuel [*Biodiesel handling and use guide, 2016*].

Cetane number: Cetane number is an indicator of the combustion speed of a diesel type fuel and the compression needed for ignition. A sufficient cetane number is needed for good engine performance. Normal diesel must have a cetane number of at least 40. [*Biodiesel handling and use guide, 2016*].

Higher Heating Value: Amount of energy released by the combustion of a unit value of fuel.

Lower Heating Value: Amount of heat released by the combustion of a sample of fuel minus the energy needed for the evaporation of its water content. Therefore, the Lower Heating Value is always less than the Higher Heating Value.

2.3 Benefits of biodiesel use

The lower contribution of biodiesel use to the rise of the net concentration of carbon dioxide in the atmosphere and minimization of global greenhouse effects can be explained by an analysis of the biodiesel life cycle. Therefore, when oilseed plants grow, they take carbon dioxide (CO_2) from the air to make the stems, roots, leaves, and seeds. After the oil is extracted from the oilseeds, it is converted into biodiesel. When the biodiesel is burned CO_2 and other emissions are released and returned to the atmosphere. Eventually, most of this emitted CO_2 does not add to the net CO_2 concentration in the air because the next oilseed crop will reuse the CO_2 as it grows. A small part of the emitted carbon is fossil derived because of fossil fuel and chemicals used in farming and in the biodiesel production process. [*Biodiesel handling and use guide, 2016*].

2.4 Advantages and disadvantages of biodiesel

Biodiesel has many major advantages, and some minor disadvantages. In Table 2 a comparison between ester biodiesel and petrodiesel main features is summarised.

Table 2. Comparison of biodiesel with petrodiesel.

Advantages	**Disadvantages**
• Biodiesel is produced from renewable sources; biodiesel fuel is a renewable energy source. • In comparison with diesel fuel, biodiesel is less toxic [*Hoekman et al., 2012*]: • Has lower emission of contaminants [*http://www.conserve-energy-future.com-2016*]; • Lower health risk. Although burning biodiesel produces carbon dioxide, it does not contribute to global warming [*http://www.conserve-energy-future.com-2016*]; • B100 can reduce carbon dioxide emissions by 78% and lower the carcinogenic properties of diesel fuel by 94% [*Azad et al., 2013*] • Biodiesel is better for vehicle engines than conventional diesel: it provides greater lubrication [*Azad et al., 2013*]; • Biodiesel have a higher flash point (100℃ minimum) than diesel (52-96℃), which make biodiesel less combustible. It is safer to store and transport.	• Biodiesel has about 10% higher Nitrogen Oxides (NO_X) content than other petroleum products. Nitrogen Oxide is one gas that is used in the formation of smog and ozone. Once it gets dissolved in atmospheric moisture, can cause acid rain [*http://www.conserve-energy-future.com-2016*]. • Biodiesel cleans dirt from the engine. This proves to be an advantage of biofuels but it is possible that this dirt may get collected in fuel filters and clog them [*http://www.conserve-energy-future.com-2016*]; • B20 blends can be used in some very cold climates, where temperatures routinely fall below -30^{0}F (1^{0}C) [*Biodiesel handling and use guide, 2016*], but biodiesel's freeze point may be 20º to 30ºF higher than that of petroleum diesel, which may cause limitations in cold weather operability.

2.5 Energy balance

According to biodiesel lifecycle studies, or energy balances, done by the United States Department of Energy, it was concluded that the production and use of biodiesel reduces 78.5% of carbon dioxide emissions, unburned hydrocarbons and particulate matter. This can be explained by biodiesel's partially closed carbon cycle [*Biodiesel Instructor-2011*] referred above. Overall, from the biodiesel energy balance (see Table 3), it can be concluded that for a unit of fossil energy needed to make biodiesel, 4.5 units of energy are gained. On the other hand, regular fossil fuels take more energy to produce than they provide in return [*http://articles.extension.org-2016*].

Table 3. Summary of Energy Balance/Energy Life Cycle [*http://dartonrefuel.com/biodiesel.php/*].

Fuel	Biodiesel	Ethanol	Diesel	Gasoline
Energy Yield*	4.50	0.805	0.843	0.805
Net Energy (Loss) or Gain (%)	350	34	15.7	19.5

* Energy Yield - Life cycle yield in liquid fuel. BTU's for each BTU of energy consumed [*http://dartonrefuel.com/biodiesel.php/*].

2.6 The biodiesel production and consumption in the world

Due to its non-toxicity and biodegradability, biodiesel has become an alternative fuel in the transportation sector, and a possible solution to environmental issues [*Hassan et al., 2013*].

The European Union is expanding its B5 (blend of 5% (v/v) biodiesel with 95% petrodiesel) blend to a B7 (blend of 7% (v/v) biodiesel with 93% petrodiesel) specification as part of the Fuel Quality Directive passed in December 2003. The renewable energy policy includes an obligatory 10% goal for transportation fuels such as hydrogen, biofuels and electricity. This new requirement updated the 5.75% renewable substitution aim of 2010, determined in 2003, to a more ambitious goal. However the 2003 aim of about 10% for biofuels in 2020 was kept as an obligatory aim. The greenhouse gas aim for biofuels to take effect in 2011 was set at a 35% decline when compared with fossil fuels. In 2017, the demand is raised to a 50% decrease, and for new producers after 2017, the aim will be 60%

[*www.biodieselmagazine.com-2016*]. In Figure 1 the investment of different countries and regions in biodiesel production is preesented [*Johanson et al., 2012*].

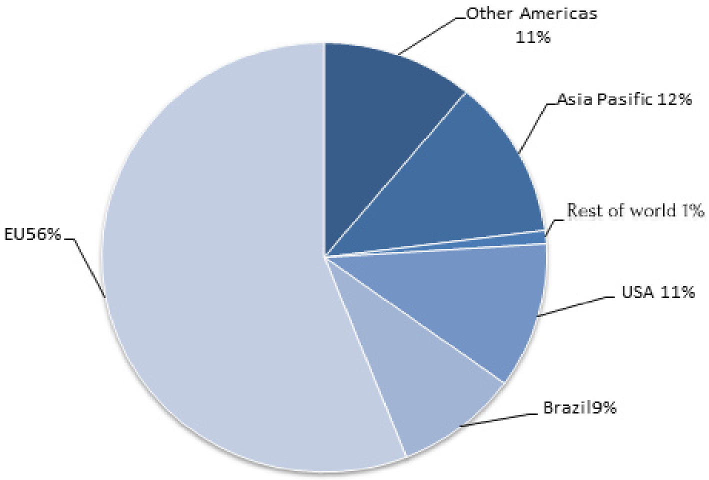


Figure 1. Biodiesel production in different countries, 2009-2010 [*Johanson et al., 2012*].

2.6.1 Biodiesel Consumption

Renewables sources have played an increasing role in the energy sector. In 2015 their contribution was €16 billion and it is projected to be €58 billion in 2030, and thanks to fast decreasing costs owing to technological advancement, especially in the power sector, renewables can also be gradually further integrated in the market. Biodiesel is the main biofuel used for transport in the EU, representing 79% of total use of biofuels in 2015. The main consumers of biodiesel are France, Germany and Italy. Renewable energy in Transport sector comes largely from biofuels (88%), with electricity playing a more limited role. In the EU, biofuels production exceeded by three times the planned trajectory, with around 3 Million tons in 2015, mainly because of the utilization of used cooking oil. The share of biofuels produced from wastes and residues, like waste cooking oils, in the EU has increased from 1% in 2009 to 23% in 2015 [*Renewable Energy Progress Report, 2017*].

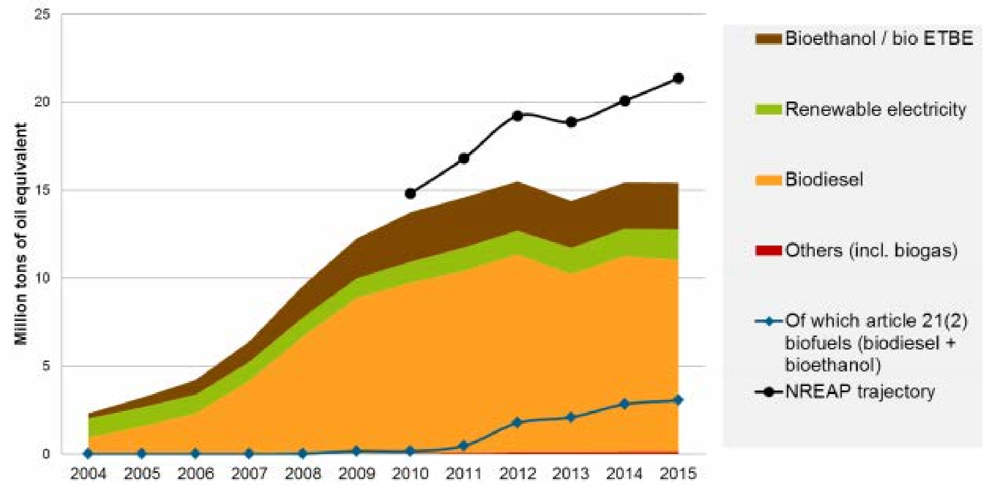


Figure 2. EU-28 renewable energy in transport, by source (source: EUROSTAT, Öko-Institut) [*Renewable Energy Progress Report- 2017*]

In EU, biodiesel consumption showed 0.5% marginal increase. In Figure 3, it is presented the production of biodiesel in Portugal after 2006. The data of 2016 to 2018 is a forecast. In Portugal the production of biodiesel from 2015 to 2016 increased 2.3% [*Phillips et al., 2016*].

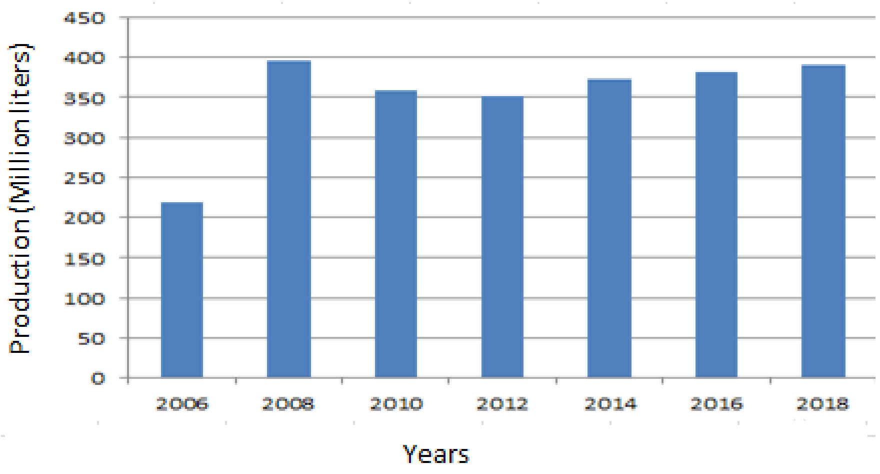


Figure 3. Production of biodiesel in Portugal 2006-2018 (Million litres) [*Phillips et al., 2016*].

2.6.2 Raw materials for Biodiesel production

Biodiesel is produced from vegetable oils all over the world. But, for biodiesel production, it can also be used animal fats, like white grease or lard, fish fat and chicken fat [*Ahmia et al., 2014*].

Figure 4 shows the relative importance of soybean oil as biodiesel feedstock in the EU and Portugal. It can be seen that soybean oil is the major feedstock in Portugal and the second in EU [*Castanheira et al., 2015*].

The most used oils for worldwide biodiesel production are rapeseed (EU), soybean (Argentina and USA), and palm (Asian and Central America) and sunflower, although other oils or fats are also used, including peanut, linseed, safflower, used vegetable oils, and animal fats [*Romano et al., 2011*].

On the other hand non-edible oil feedstocks range from castor oil to jatropha, tung, cotton, jojoba and microalgae oils, which proved to be highly promising and reliable sources, having high oil content. Algae oil, due to its availability and low cost is considered as an economical choice for biodiesel production [*Gashaw et al., 2014*].

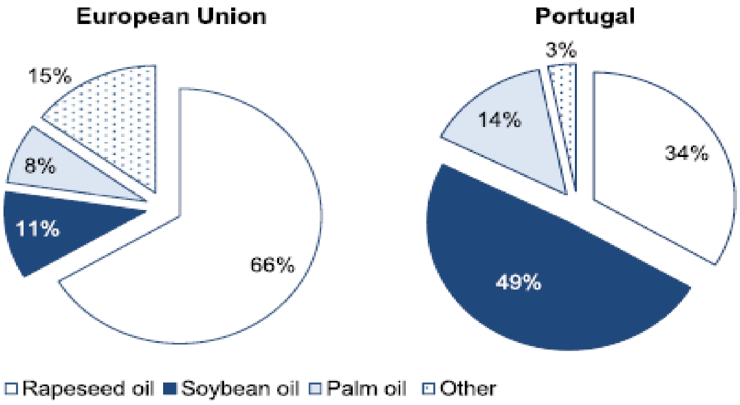


Figure 4. Feedstock used for biodiesel production in the European Union and Portugal [*Castanheira et al., 2015*].

Microalgae, a large and diverse group of aquatic organisms that lack the complex cell structures found in higher plants [*Slade et al., 2013*], appear to be a very important alternative for future biodiesel production due to its potential oil yield; however, its application for biofuel production is still commercially limited [*Romano et al., 2011*], due to the highly energetic intensive technologies available for algae oil recovery.

2.7 Production of biodiesel

The recent interests in biodiesel reside in the regular rises in oil prices and the disappearing resources of fossil fuels. These issues boosted the interest in biodiesel production from both animal and vegetable fats. In fact, intensive usage of petroleum based materials and fuels are an important factor in air pollution: an extremely important problem, as mankind may face a global warming crisis [*Earle et al. 2009*].

Ester biodiesel, which is a mixture of Fatty Acid Methyl Esters (FAME), is made through the transesterification of animal fat or vegetable oils. Fats are mainly constituted by mixtures of triglycerides, which are triesters of glycerol, molecules with a glycerol core connected to 3 fatty acid chains by ester groups. The most important fatty acid ester derivative is oleic acid, but oils usually exhibit smaller contents of fatty acid saturated chains (of varying lengths) and some double unsaturated chains (like linoleic acid ester derivatives). For fatty esters, both acid- and base-catalysed transesterifications reactions are possible. However, base catalysed transesterification to methyl or ethyl esters usually require slightly higher reaction temperatures [*Earle et al., 2009*].

Biodiesel can also be produced by esterification of free fatty acids (FFAs) derived from vegetable oils, with separation of the water by-product from the FAME product. For fatty acids, the acid-catalysed esterification reaction is preferred. The base-catalysed esterification to methyl and ethyl esters is not used because the catalyst is deactivated by reaction with the carboxylic acid group to form a carboxylic acid salt, which is often called soap [*Earle et al., 2009*].

Table 4 summarizes the biodiesel production processes: FAME is produced from vegetable oils, animal fats or waste cooking oils by transesterification. In the transesterification process a triglyceride reacts with an alcohol in the presence of a catalyst, forming a mixture of fatty acids esters and another alcohol. Using triglycerides results in the production of glycerol as a by-product [*http://www.biofuelstp.eu - 2016*]. On the other hand, vegetable oils and animal fats, which are typically branched or straight chain molecules, may also be hydrotreated in order to de-oxygenate the fatty acids and saturate any double bonds, producing paraffinic hydrocarbons. Synthetic diesel and gasoline can also be produced by gasification of dried wood, agriculture residues, straw, corn, garbage, food scraps, and sewage-sludge into synthesis gas, which is subsequently converted to hydrocarbon liquid products by Fischer-Tropsch processes. The overall processes are often called biomass to liquids (BTL) [*Biomass Gasification Facility for Clean Synthetic Diesel Fuels - 2009*].

Table 4. Methods for biodiesel production [*Pacini et al., 2014*].

Process	Feedstock	Product
Transesterification	Vegetable oils and animal fat	Fatty acidy methyl ester (FAME)+Glycerol
Hydrotreating	Vegetable oils and animal fat	Hydrotreated vegetable oil (HVO)+ Paraffin
Gasification +Fischer Tropsch	Wood, energy crops, agriculture residues, waste etc.	Biomass to liquid fuel(BTL)

2.7.1 Esterification and Transesterification

The esterification process is used for the biodiesel production from free fatty acid. Esterification is the process of forming esters from carboxylic acids. Esterification occurs when a carboxylic acid reacts with an alcohol. The overall esterification process takes place according to the chemical equation shown in Figure 5.

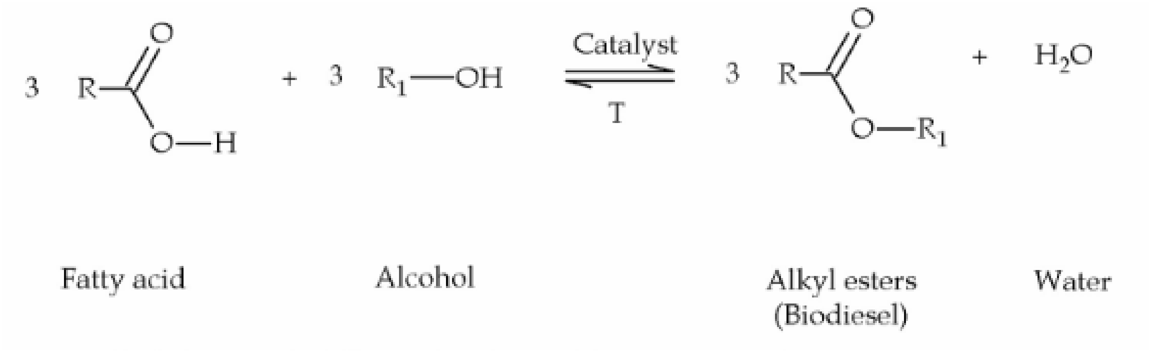


Figure 5. Biodiesel synthesis by esterification process from Free Fatty acid with alcohol [*Maria et al., 2011*].

In Figure 6 basic technology of biodiesel esterification process.

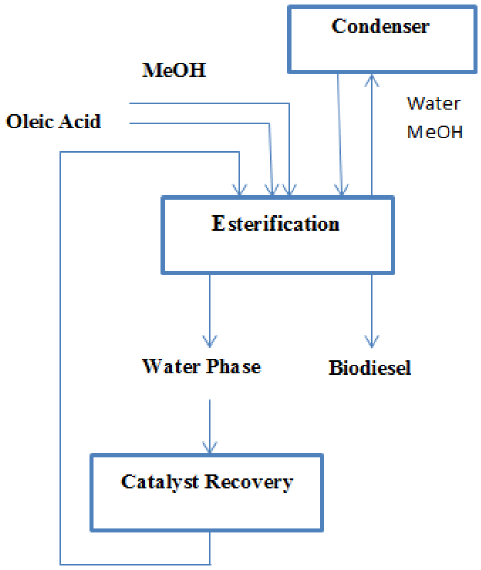


Figure 6. Basic technology of biodiesel esterification process.

As stated above, the most used industrial process for ester biodiesel production is transesterification. This reaction of an alcohol with an ester to produce another alcohol and ester is a conversion process similar to hydrolysis, except that an alcohol is used instead of water. Suitable alcohols include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol is most frequently used, because of its low cost and its physical and chemical advantages [*Hideki et al., 2001*].

In this process, a three step reaction mechanism is assumed, where triglycerides and monoglycerides act as intermediates. The overall transesterification process occurs according to the chemical equation shown in Figure 7.

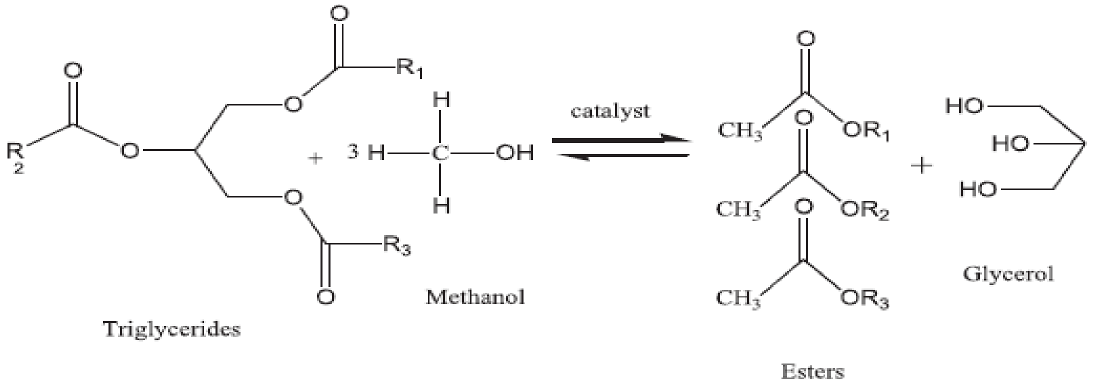


Figure 7. Biodiesel synthesis by transesterification process from vegetable oils with methanol [*Ullah et al., 2014*].

Considering a base catalysed process, an amount of alkali (for example NaOH) slowly dissolves in alcohol excess (usually methanol). This methoxide mixture is mixed with warm preheated oil at about 50°C, and allowed to react for 1 to 8 hours to ensure a complete transesterification reaction. In pressurised conditions, the reaction mixture may be maintained above the alcohol boiling point (70°C), but for normal pressure systems, it is recommended to maintain the temperature range from room temperature to 55 °C, for safety reasons. Under normal pressure conditions, the reaction time is usually from 1 to 10 hours, and it is important to avoid a sealed system in order to prevent the risk of explosion, because the reaction rate is doubled by raising the reaction temperature by 10 °C. In pressurised conditions and to prevent evaporation of the alcohol, the reaction should be carried out in a closed container [*www.bioethanol.ru-2016*] or using a reflux process. In Figure 8 it is shown the basic technology for ester biodiesel production.

The use of mineral acids in acid catalysed processes has some disadvantages such as equipment corrosion, long workup procedure and environmental problems. Recently, replacement of these hazardous liquid acids by solid acid catalysts has been essential, but these catalysts show also some disadvantages such as low activity, easy deactivation and adsorption/desorption of products [*Aghabarari et al., 2013*].

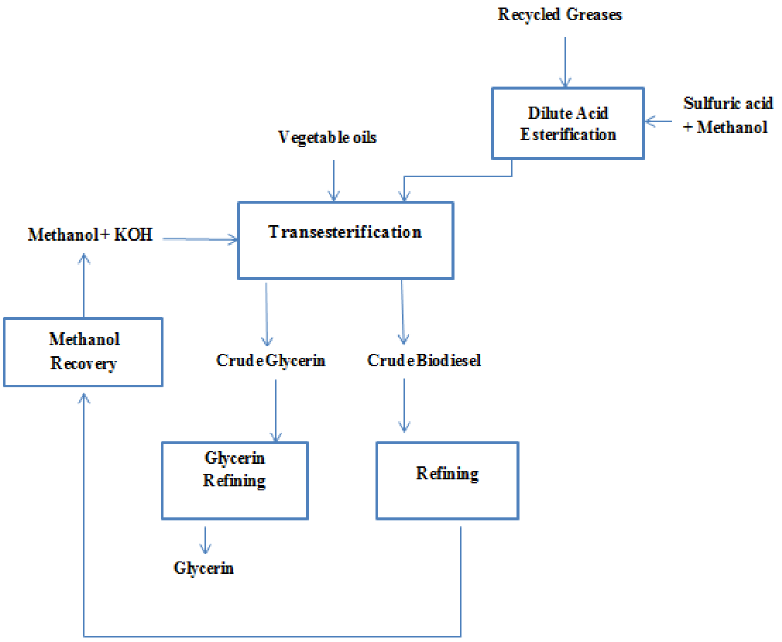


Figure 8. Basic technology of biodiesel transesterification process [*www.bioethanol.ru-2016*].

3 Ionic liquids

An ionic liquid is a molten salt consisting of a cation and an anion, with low melting temperature. The earliest discovery of ionic liquids (ILs) was in the mid nineteenth-century when “red oil”, generated by Friedel-Crafts reaction, was used as a solvent for separation analysis. In 1914 Paul Walden reported the first widely-known ionic liquid, ethyl ammonium nitrate. Interest in the study of ionic liquids became more intense in 1963, after the research project of Major (Dr.) Lowell A. King of the US Air Force Academy. Later, in 1990, the professor from US Air Force Academy, Dr. Mike Zaworodko discovered the solution for the problems faced by Dr. King which gave a new dimension for using of ionic liquids in electrochemistry. Since then, due to its unique properties and possible uses, ILs drew the interest of scientific researches and even several industries [*Terencia et al., 2010*].

ILs consist of ions and remain liquid at temperatures lower than 100 °C. Typical IL cations are nitrogen-containing (such as alkylammonium, N-dialkylimidazolium, N-alkylpyridinium and pyrrolidinium), or phosphorous containing (such as alkylphosphonium). The common choices of anions include halides, BF_4^- , PF_6^- , $CH_3CO_2^-$, $CF_3CO_2^-$, NO_3^- , Tf_2N^- [i.e.,$(CF_3SO_2)_2N]^-$, $[RSO_4]$ and [R2PO$_4$] [*Zhao et al., 2012*]. The overall properties of ILs derived from the composite properties of the cations and anions and include those that are superacidic, basic, hydrophilic, water miscible, and water immiscible and hydrophobic. The anion is currently used to control the water solubility, but the cation can also influence the hydrophobicity or hydrogen bonding ability [*Huddleston et al., 2001*]. Some cations and anions are shown in Figure 9.

Imidazolium-based ionic liquids have been used as green solvents to replace the volatile and relatively toxic organic solvents, in homogeneous and heterogeneous catalysis, materials science, nano materials, lithium ion batteries, and separation technology. Imidazolium based ionic liquids, because of its inherent ionic patterns, low pressure and ability of self-organization in different states, are considered as the most studied species [*Woon et. al., 2012*].

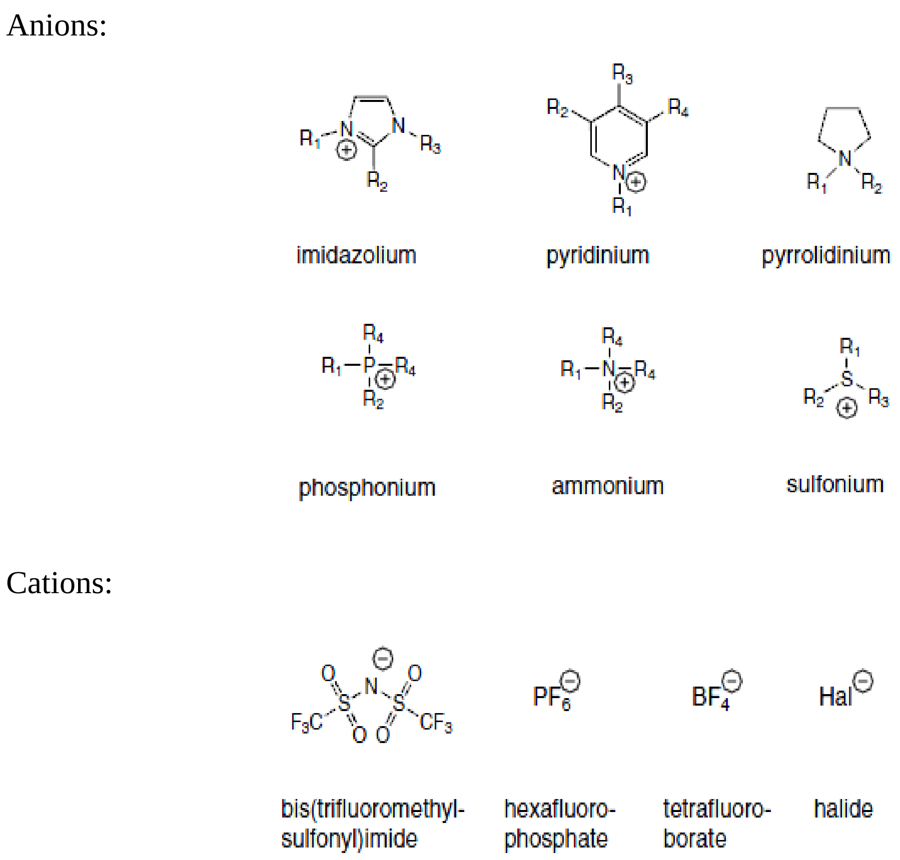
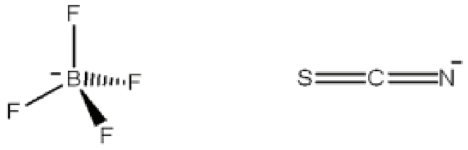


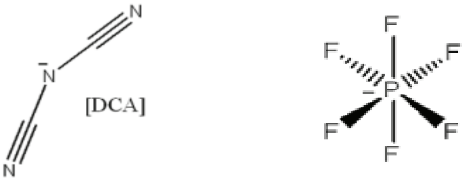
Figure 9. Chemical structure of ionic liquids [*http://www.sigmaaldrich.com-2016*].

3.1 Classification of ionic liquids

Ionic liquids are good solvents, environmentally benign, nonvolatile, nonflammable, and stable in air or water. Because of these special properties, ionic liquids have been widely investigated as solvents for synthetic chemistry and catalysis [Zhang et al., 2007]. Ionic liquids are generally divided into two broad classes, one based on chlorometallate anions such as heptachlorodialuminate ($[Al_2Cl_7]^-$) and the other based on anions not containing metals, such as hexafluorophosphate ($[PF_6]^-$) [*Andreani et al., 2012*]. There are a large number of imidazolium-based ILs, few ILs based on quaternary ammonium have been reported. Quaternary ammonium salts ("quats") because of its surface-active properties, possess anti-microbial activity are an economically advantageous class of industrial compounds. Most of these solvents remove lignin and alter cellulose structure, which increases the accessibility of cellulolytic enzymes [*Visser et al., 2007*].



Tetrofluoroborate
Thyocyanate



Dicyaneamide
Hexafluorophosphate

Figure 10. Selected anions of phosphonium- and ammonium-based ILs [*Stojanovic et al., 2011*].

ILs plays a crucial role when applied as solvents or catalysts for different reactions at high temperatures, or if the reaction products should be distilled from the ionic liquid at high temperatures Ammonium and phosphonium ILs both can decompose at elevated temperatures, but phosphonium salts are generally more stable as their ammonium analogs [*Stojanovic et al., 2011*].

In this work different Ionic Liquids, were studied, with structures presented in Figure 11.

1-Butyl-3-methylimidazolium chloride
1-Butyl-3-methylimidazolium hydrogen sulfate

1-Butyl-3-methylimidazolium methyl sulfate
Tributylmethylammonium methyl sulfate

1-Methylimidazolium hydrogen sulfate
1-Butyl-3-methylimidazolium methanesulfonate

Figure 11. Structure of different ILs

3.2 Ionic liquid properties

ILs has many positive properties such as low flammability, high ionic conductivity, high thermal conductivity, high dissolution capability toward many substrates, high thermal and chemical stability [*Zhao et al., 2012*]. The ionic liquids possessed greener properties such as significantly less toxic compared to the organic solvent. In addition, they can be colourless, have high catalytic activity, low viscosity, potential recyclability, and are easily manipulated. The highly interesting characteristic of ionic liquids is the ability of designing a molecule, target for a particular application or in order for getting a certain set of properties such as melting point, viscosity, density, water solubility and selectivity [*Andreani et al., 2012*]. ILs contains large, organic cations with a variety of anions and melts at or below about 100 °C [*Huddleston et al., 2001*]. The active research of ILs as alternative solvents and catalysts in the chemical or enzymatic (biocatalytic) production of biodiesel has gained momentum [*Hua et al., 2013*]. The first industrial process involving ionic liquids was announced in March, 2003, by BASF, and is called BASIL (Biphasic Acid Scavenging Using Ionic Liquids). This process generates an ionic liquid in situ to remove HCl formed during the production of alkoxyphenylphosphines. The resultant alkoxyphenylphosphine is used as an important precursor for the synthesis of photoinitiators used in various industrial processes. The ionic liquid is separated from the product and can be removed by decantation, presenting advantages of cost and easiness compared to filtration. The use of ionic liquids increases the yield of this process by a factor of 80,000 compared to the conventional process [*Andreani et al., 2012*]. ILs have great chemical and thermal solubility which is also tuneable based on the combination of cation and anion. For biodiesel synthesis, the ILs is capable of dissolving a wide array of substrates and more importantly, increasing their stability over a longer period during the reaction. The ionic liquids (ILs) offer an excellent media for many lipase-catalysed esterification or transesterification reactions compared to the organic solvents wherein an increased in the activity and specificity of the lipase enzyme was spotted. Many recent studies, proved the ILs as more environmental friendly solvents and catalysts for biodiesel reactions and separation [*Muhammad et al., 2015*].

Ionic liquids can be used as single catalysts in the processes of biodiesel production, either by esterification or transesterification, provided that some ionic liquids present Bronsted acidity or basicity.

Bronsted acidic ILs, were highly efficient catalyst for biodiesel synthesis from vegetable oils. Sulfuric acid groups in these ILs are the active sites for transesterification [*Guo et al., 2011*].

Currently, there are several scientific works published about the production of biodiesel using ionic liquids. Some of these works are referred in Table 5.

- Ren and co-workers studied the production of biodiesel using as catalyst [Hnmm] OH, a basic ionic IL. The raw material used was soybean oil. They analysed several reaction parameters such as the influence of catalyst concentration on the biodiesel yield, the effect of methanol / soybean oil molar ratio and the effect of reaction time. The authors found out that the catalyst had an excellent catalytic performance at 70 °C reaction temperature, 1.5 h of reaction time, 3% wt catalyst dosage and a molar ratio of MeOH/oil = 8/1. The obtained reaction yield was about 90% [*Ren et. al., 2014*].
- In 2011, the production of biodiesel was studied by Guo *et al.*, using as catalyst $[BMIM][CH_3SO_3]-FeCl_3$ and $[BMIM][CH_3SO_3]-AlCl_3$, a basic ionic IL. The raw material used was Jatropha oil. At high temperature of 120 °C, the reaction time 5 h. Fe^{3+} had a relatively higher activity than that of Al^{3+} (99.7% vs. 94%).
- Using palm oil and $BMIMHSO_4$ as catalyst, a reaction temperature of 160 ºC, 1 h for the reaction time and 1% wt of catalyst, [*Elsheikh et al., 2011*], obtained a reaction yield of 98.4%.
- In another experiments from Fang and his colleagues different catalysts $[C_4MIM]$ $[NTf_2]$ and $[C_2MIM][TfO]$ were used for production of biodiesel. During all experiments raw material used Soybean oil. The first experiment was at room temperature, second experiment was at 50 °C and reaction time is 12 h. The reaction yield was 96 % and 80 % [*Fang et al., 2014*].
- For production biodiesel is used triolein oils with different catalysts ($[C_{18}MIM][NTf_2]$ and $[C_{16}MIM][NTf_2]$), a basic ionic IL. The process was doing in the same temperature (60°C). The one experiment was a 6 h; another experiment was a 24 h. The reaction yield was 96 %, 99% [*Fang et al., 2014*].
- The production of biodiesel from waste cooking oil was studied by Ullah and co-workers. They used as catalyst $BMIMHSO_4$, a basic ionic IL. The catalyst was efficient in the first hour of reaction with the yield reaching up to 95.65%. After that there was no considerable change in the yield, therefore the reaction time of 1 h was

identified as the optimum reaction time, at high temperature of 160 °C [*Ullah et al.,2015*].

Table 5. Recent published studies using different oils and ionic liquids for biodiesel production. Effect of reaction and time reaction on production yield

Oils	**Ionic Liquids**	**T(℃)**	**Time(h)**	**Yield(%)**
Soybean oil [*Ren et al., 2014*]	[Hnmm]OH	70	1.5	97
Jatropha oil [*Guo et al.,2011*]	[BMIM][CH_3SO_3] –$AlCl_3$	120	5	94
Jatropha oil [*Guo et al.,2011*]	[BMIM][CH_3SO_3] –$FeCl_3$	120	5	99.7
Crude palm oil [*Elsheikh et al.,2011*]	$BMIMHSO_4$	160	1	98.4
Triolein [*Fang et al.,2014*]	[C_{18}MIM][NTf_2]	60	6	96
Myglyol oil [*Fang et al.,2014*]	Cholrine acetate	40	3	97
Cooking oil [Fang *et al.*,2014]	1ethyl,3methyl Imidazolium trifluromethane sulfonate	40	24	99
Soybean oil [*Fang-2014*]	[C_4MIM][NTf_2]	Room Temperature	12	96
Triolein [*Fang et al.,2014*]	[C_{16}MIM][NTf_2]	60	24	99
Soybean oil [*Fang et al.,2014*]	[C_2MIM][TfO]	50	12	80
Waste Cooking Oil [*Ullah et al.,2015*]	[BMIM][HSO_4]	160	1	95.65

3.3 The role of ionic liquids in transesterification reactions

In biodiesel production from vegetable oils and animal fats, depending on the catalyst used, there are specific characteristics related with these reactions. For example, acid catalysts are mainly used when the oil has a high concentration of free fatty acids, with sulphuric and sulfonic acids as the most common catalysts of this class. As disadvantages, the acid catalysis requires the use of large amounts of alcohol additionally; acid catalysts such as sulphuric acid catalyse the transesterification of triglycerides slowly even when refluxing with methanol, leading to long reaction times such as 48-96 hours. And there is the risk of corrosion of the equipment used due to the high acidity of those catalysts [*Adreani et al., 2012*].

Ionic liquids are more expensive than conventional solvents and catalysts used in chemical reactions. Two of the most commonly used ionic liquids are 1-n-butyl-3-methylimidazolium tetrafluoroborate ([BMI][BF_4]) and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF_6]) [*Andreani et al, 2012*]. But the use of ionic liquids in catalytic systems seems to be environmentally secure. The possibility of recovery and reuse of ionic liquids minimizes the waste in catalytic reactions. Ionic liquids have been using in most number of chemical reaction types. The important advantage of using ionic liquids in reactions is their non-volatility except at high pressures and low temperatures. ILs possesse numerous advantages over the conventional organic solvents (they possessed greener properties such as very low relative volatility i.e., wide liquid temperature and significantly less toxic compared to the organic solvent). More important is their ability to selectively dissolve various organic, inorganic, and organometallic materials due to their tuneable polarity which can be designed for specific purposes. In view of the environmental friendly nature of ILs, the catalyst also referred to as green catalyst. ILs is considered prospective catalysts for biodiesel production. Using ILs based catalyst could reduce the number of reactions and purification steps required in the biodiesel preparation and separation hence rendering the process to be more economically competitive [*Muhammad et al., 2015*].

3.4 Ionic Liquids recovery

In nowadays ILs can be used for developing new processes that are technologically, environmentally and economically advantageous. However ILs has typically high costs. So, for an improvement in the economic, efficiency the recycling and reuse of ILs are critical. Also, recovery of ILs is important to minimise the environmental concerns of the disposal, like biodegradation and toxicity (they can be mixed with other products). Even though ILs is considered as homogeneous catalysts because they are in the same phase as the reactants, its capability to be recovered and recycled is an advantage over conventional homogeneous solvents. For the recovery and recycle of ILs the most used method is distillation, because ILs show low vapour pressures. It is important to note that the interaction of ILs with water, which is mainly affected by the size of ILs, hydrophobicity and hydrogen bonding ability of both cations and anions, will determine the techniques used for its recovery. Among these effects, the nature of anions largely determines the behaviour of the IL-water mixture. Hydrophobic ILs which is immiscible with water can be easily separated from water by decantation. Additionally, many molecular solvents including water are immiscible with ILs and can be used to extract or separate materials from the IL solutions [*Freire et al., 2007*].

For the recovery of ILs there are used different methods

- Distillation is the simplest method for the recovery of ILs. First ILs is removed by decantation, filtration and/or extraction, and also by washing with water/organic solvents. After that, distillation can be used for recycling and reuse of ILs [*Mai et al., 2014*]. For example [BMIM][$FeCl_4$] IL is heated in the oven at 105 ºC for 24 h to evaporate water [*Fauzi et al., 2014*]. For recovery of [BMIM][HSO_4], it is washed with distilled water to remove any impurities, and afterwards heated in the oven at 105 ºC for 24 h to remove traces of water and unreacted methanol [*Fauzi, 2014*]. [HMIM][HSO_4] can be used in the ester exchange reaction after washing with ethyl acetate; excess ethyl acetate was removed by reduced-pressure distillation. It was found that [HMIM][HSO_4] recycled 4 times can still retain stable catalytic performance [*Xu Wei et al., 2015*]. Adsorption can be used for retaining ILs onto solid supports such as activated carbon (AC), silica (SiO_2), alumina (Al_2O_3), titanium dioxide (TiO_2), and clays [*Mai et al., 2014*].
- After reaction the water was added to the reaction mixture and then the solid was isolated by filtration. The IL in water could be recovered easily by evaporation at 80 ºC in a vacuum. The recovered IL was washed with diethyl ether and dried at 80ºC in a vacuum for 1h [*Abbaspour-Gilandeha, 2014*].
- An alternative method for recovery ILs which does not use high thermal application is extraction of IL using carbon dioxide. Blanchard and Brennecke demonstrated the separation of an ionic liquid ([BMIM] [PF_6]) from a number of organic compounds using supercritical carbon dioxide ($SCCO_2$) extraction method. The method is effective because organic compounds are soluble in CO_2, while ILs is insoluble. This

enabled the separation of organic compounds from IL, and depressurization is then applied to remove solutes from CO_2 [*Fauzi et al., 2012*].

- Recovery of ILs can also be performed by crystallization processes. Using this method, crystals of ILs are easily separated from the reaction mixture as they are in different phases. The temperature at which the IL solidifies are important in this method. Hayyan studied the use of 1-butanol as an anti-solvent for the separation of choline chloride from glycerin after the transesterification process. After the introduction of the anti-solvent into the glycerin phase, the temperature was reduced to -20 °C, and the crystals of choline chloride were separated. Further filtration under vacuum was required to recover the IL [*Fauzi et al., 2012*].

In Table 6 recent published studies are shown involving ILs recovery for reactions of biodiesel production, using different oils and ionic liquids, emphasizing the effects of reaction and time reaction on production yield.

Table 6. Recent published studies involving ILs recovery for reactions of biodiesel production, using different oils and ionic liquids

Ionic liquid	Raw material(s)	Number of runs	Initial conversion (C)/yield (Y) %	Final conversion (C)/yield (Y) %
$[PSPy][HSO_4]$	Benzoic acid	4	88 (Y)	88 (Y)
$[NMP][HSO_4]$	Methyl acetoacetate	4	80 (Y)	75 (Y)
$[MIM][BF_4]$	Acetic acid	4	90 (Y)	86 (Y)
$[(CH_2)_4SO_3HMIM][CF_3SO_3]$	n-butyric acid	4	93 (C)	91 (C)
$[(CH_2)_4SO_3HMIM][HSO_4]$	Acetic acid	5	93 (C)	89 (C)
$[NMP][CH_3SO_3]$	Acetic acid	6	95 (C)	93 (C)
$[NMP][CH_3SO_3]$	Oleic acid	8	95 (C)	91 (C)
$[HMIM][BF_4]$	Acetic acid	8	97 (C)	94 (C)
$[HSO_3\text{-}pMIM][HSO_4]$	Glycerol	10	96 (Y)	92 (Y)

4 Experimental

4.1 Introduction

The first experimental task of this work was the selection of a suitable ionic liquid in order to study the effect its recovery and use in a set of 4 or 5 consecutive esterification reactions. All the 5 ILs available in the LQA laboratory were tested and only one IL was chosen. Then, several esterification reactions were performed using three different amounts (%) of ionic liquid. After each reaction, the obtained samples were separated in aqueous and organic phases by decantation and centrifugation. Both organic (biodiesel) and aqueous (with ionic liquid) samples were dried and stored in the refrigerator (4 ºC) for further analysis. After each reaction test, the reaction yield was determined using the acidity of the organic phase measured by volumetric titration. The characterization of the produced biodiesel samples was measured qualitatively and quantitatively by determination of Fatty Acid Methyl Esters content by the Gas Chromatography (GC). Additionally, initial and final samples of the selected ionic liquid were characterized by UV-Vis and FT-IR spectroscopy.

4.2 Chemicals and Equipment

Oleic acid (cis-9-octadecenoic acid) (≥90%) was purchased from Fluka and heptadecanoate methyl ester (≥97%), used as internal standard in the GC analysis was obtained from TCI Company, Japan. Five different ionic liquids: 1-butyl-3-methylimidazolium hydrogen sulfate (≥94.5%), 1-butyl-3-methylimidazolium methyl sulfate (≥95%), 1-methylimidazolium hydrogen sulfate (≥95%), 1-butyl-3-methylimidazolium methansulfanate (≥95%) were purchased from Sigma-Aldrich, Switzerland and the tributylmethylammonium methyl sulfate from Chem Cruz Company, United States. It was also used: Methanol (≥99.9%) from Carlo Erba; heptane (≥90%) from Fluka; potassium hydroxide from Riedel-deHaen; hydrochloric acid (≥37%) from Fisher; Ethanol (absolute) and diethyl ether (≥99.8%) from Carlo Erba; and sodium tetraborate and anhydrous sodium sulfate were obtained from Carlo Erba. 37 FAME mix standard solution from Supelco, and sulfuric acid (≥95.0-97.0%) from Sigma-Aldrich, Switzerland, were also used.

The chemical formula and molecular weight of oleic acid and the 5 ionic liquids studied in this work are presented in Table 7.

Table 7. Chemical formula, density and molecular weight of oleic acid and the 5 ionic liquids.

Name	**Chemical formula**	**MW (g/mol)**
Oleic acid	$C_{18}H_{34}O_2$	282.46
1-Butyl-3-methylimidazolium hydrogen sulfate	$[BMIM][HSO_4]$	236.29
1-Butyl-3-methylimidazolium methyl sulfate	$[BMIM][MeSO_4]$	250.32
1-Methylimidazolium Hydrogen sulfate	$[MIM][HSO_4]$	180.18
1-Butyl-3-methylimidazolium methanesulfonate	$[BMIM][CH_3SO_4]$	234.32
Tributylmethylammonium methyl sulfate	$C_{14}H_{33}NO_4S$	311.48

The characterization of biodiesel samples was performed using a VARIAN CP-3800 Gas Chromatography system equipped with a FID detector. For ILs characterization (before and after recovery) a Barnstead Lab Line 3618-5 Vacuum Oven from Thermo Scientific, a VARIAN Cary 50 UV-Vis and a FT-IR ABB model MB3000 spectrophotometers were used.

4.3 Biodiesel Production by Esterification Reaction

The esterification reaction was carried out in a 100 mL glass reactor with continuous stirring, connected to a reflux condenser and a thermometer (Figure 12). The methanol and oleic acid (1:10 molar ratio), in this order, were added into the glass reactor. The reactor containing the mixture was then immersed into a paraffin bath. The reactor was then heated until a temperature of 90°C and methanol was added to the reactor.

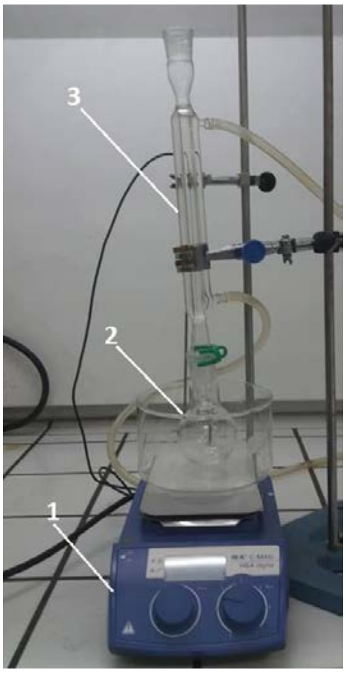


Figure 12. Experimental setup for the esterification: 1) Heater 2) Reactor 3) Condenser.

The reaction was stopped after 6 hours and then the reactor was cooled to room temperature. It was verified the formation of a single phase inside the reactor. After cooling, the mixture was removed from the reactor and transferred into centrifugal tubes (Figure 13). Then the mixture was centrifuged during 20 minutes at 3000 rpm and the samples inside the tubes were stored in the fridge (4 ºC).

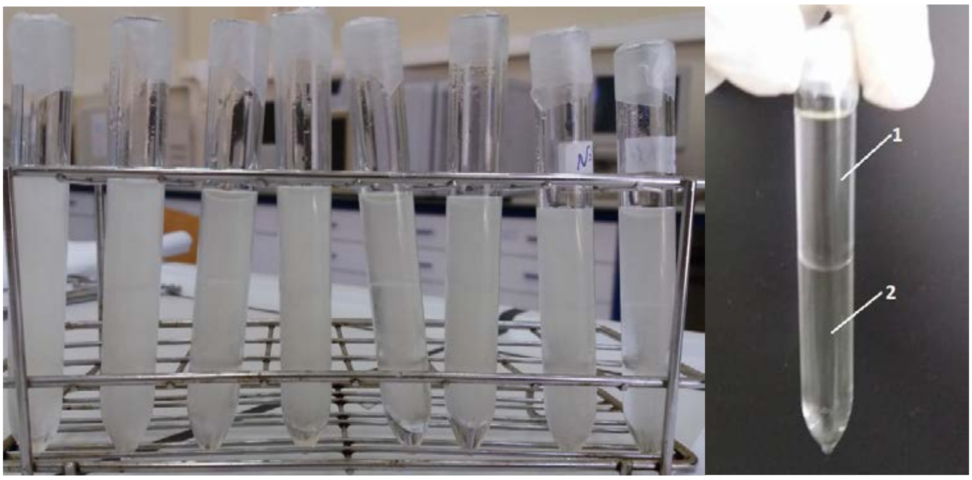


Figure 13. Tubes with the mixture after reaction: 1) Organic phase 2) Water phase.

After 24 h into the fridge, the mixture was able to separate into two phases. The phases were separated using a pipette and the mass of each phase was measured using an analytical balance Adam Equipment ADA-210/I Balance.

Both phases were then stored in 10 mL brown flasks inside the fridge for further analysis: acidity determination, and characterization by GC, UV-Vis and FT-IR.

4.4 Recovery of ILs

In this work the esterification reaction was studied for biodiesel production using ILs as catalysts. The reactions were carried out with three different [BMIM][H_2SO_4] amounts (10%, 15% and 20% wt). In each reaction the IL samples were recovered and reused in a following reaction test maintaining the same IL amount relating to the initial oleic acid weight. 4 runs were done in 10% reaction sequence, and for 15% and 20% reactions sequences, 5 runs were done. The recovery procedure is described below:

a. After 2 days from the reaction test, the separation of phases were concluded (see Figure 14);
b. The organic phase (biodiesel) was analysed by calculating its acidity;

Figure 14. Separation Phases.

c. The water phase was treated by evaporation for IL recovery: first it is heated for 1 hour at 110 ℃ afterwards the sample is introduced in a vacuum oven at 60℃ for 12-15 h (see Figure 15).

Figure 15. Vacuum oven.

After evaporation, the ILs were recovered and used for the next reaction. In Figure 16 there are presented examples of phases before and after IL recovery for the 15% and 20% runs.

a) Before Recovery b) After Recovery

Figure 16. ILs samples before and after recovery.

4.4.1 Biodiesel Acidity Measurements

For biodiesel analysis a titration method was used (Method EN 14104:2003). First, an HCl 0.1M solution was prepared and standardized with borax. Then, a KOH alcoholic 0.1 mol/L solution was prepared and its concentration was checked with the standardized HCl solution. After that 1L of solvent (Ethanol/Diethyl ether 1/1) was also prepared and the standardized solution of KOH was diluted to a 0.01M concentration. These solutions were used for the determination of the acidity of oleic acid and biodiesel samples.

a) Determination of acidity of oleic acid/biodiesel (with alcoholic solution of KOH)

For volumetric titration diethyl ester/ethanol 1:1 (v/v) solution was used as the solvent and phenolphthalein was used as the indicator. First 40 mL of solvent were titrated adding 5 drops of phenolphthalein and stirring the mixture while the KOH standard solution was added from the burette in order to neutralize the solution until the color changes to light pink. After that 1 mL of biodiesel sample was weighed using a precision balance, and titrated with the same solvent, until achieving pink color.

The acidity of the samples is determined by equation 1.

$$Acid\ value, AV\left(\frac{mg\ KOH}{g\ biodiesel}\right) = \frac{V*C_{KOH}*M_{W(KOH)}}{m_{biodiesel}} \quad (1)$$

where:

V - Volume of KOH standard solution needed to titrate the sample (mL)

$\mathbf{C_{KOH}}$ - Concentration of potassium hydroxide standard solution (KOH) (mol/L)

$\mathbf{M_{W(KOH)}}$ - Molecular weight of KOH = 56.1 (g/mol)

$\mathbf{m_{biodiesel}}$ - Weight of sample (g).

b) Determination of the biodiesel yield

The produced biodiesel is a result from the reaction between oleic acid and methanol, in the presence of a catalyst (IL). Biodiesel is constituted by methyl esters. The yield of the esterification reaction can be quantified by determining the acidity level according to equation (2):

$$yield\ \% = \frac{A_i - A_f}{A_i} * 100 \quad (2)$$

where:

$\mathbf{A_i}$- Acidity of oleic acid (initial), ($mg_{KOH}/g_{oleic\ acid}$),

$\mathbf{A_f}$- Acidity of sample (final) after reaction, ($mg_{KOH}/g_{biodiesel}$).

4.5 Analysis of Fatty Acid Methyl Ester (FAME) Content by Gas Chromatography

For the determination of FAME content of all biodiesel samples a VARIAN CP-3800 gas chromatography equipment was used (see Figure 17). The system has a FID detector (Flame Ionization Detector) and a Supelcowax-10 capillary column (30mx0.25mmx0.25µm). The conditions used for analytical method were:

- Helium flow-rate (carrier gas): 1 mL/min
- Oven: 50 ^{0}C (2 min); 4 ^{0}C/min until 220 ^{0}C (total running time: 80 min)
- Injector temperature: 250 ^{0}C (split ratio 1:5)
- Sample volume: 1 µL

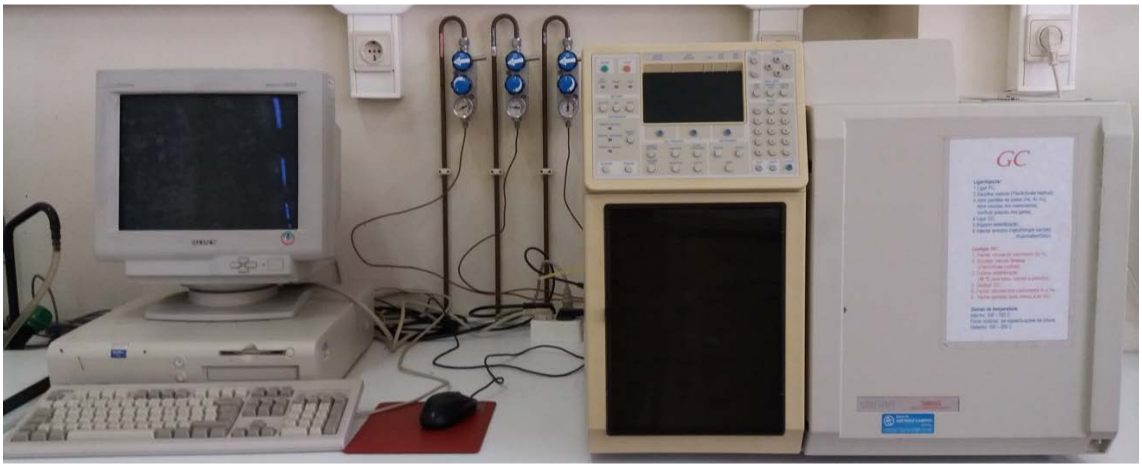


Figure 17. The VARIAN CP-3800 gas chromatography system.

4.5.1 Identification of FAMEs Compounds Methodology

The chromatogram obtained for the GC analysis using the Supelcowax-10 column of the standard mixture is presented in Figure 18.

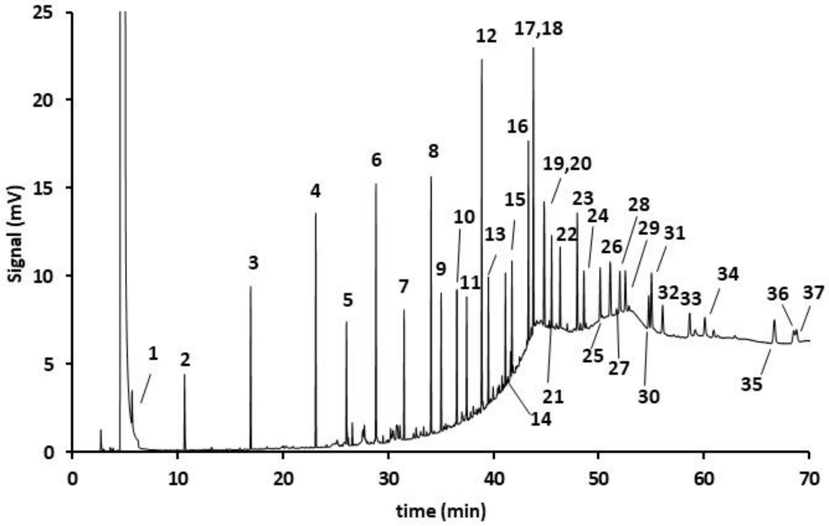


Figure 18. GC chromatogram obtained for the Supelco 37 FAME standard mix using a Supelcowax-10 column.

The elution order (numbers in the chromatogram) and the retention time of each one of all the 37 methyl esters compounds present in the standard mixture were obtained by comparison with the analysis using an Omegawax 250 column (similar stationary phase) already published by Sigma-Aldrich (Supelco Bulletin 907). This chromatogram, used as reference, is showed in Figure 19.

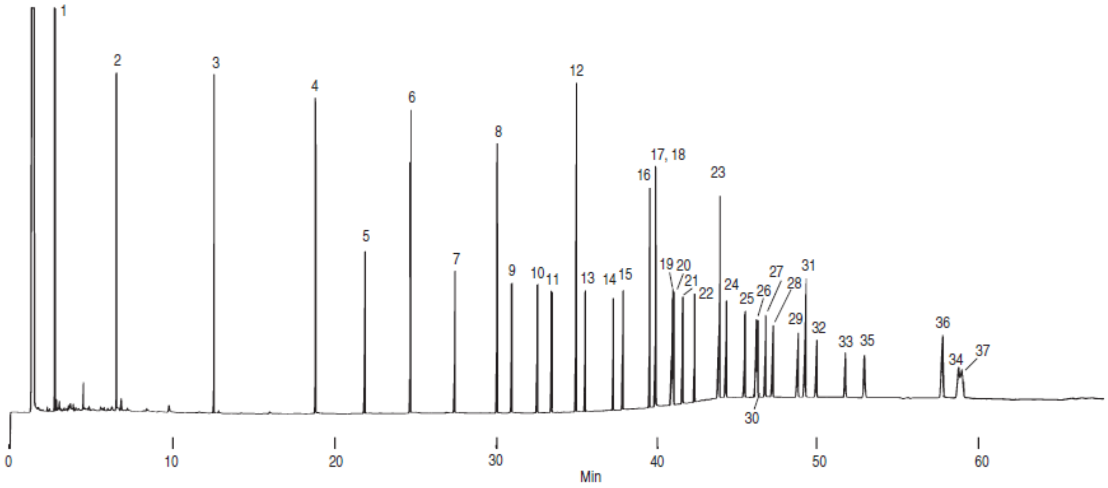


Figure 19. GC Chromatogram obtained for Supelco 37 Component FAME Mix on Omegawax 250 Column (Supelco Bulletin 907).

Comparing both chromatograms it is possible to identify the retention time (and elution order) for the 37 FAMEs, as it is presented in Table 8.

Table 8. Identification of the retention time of all the 37 compounds of the Supelco FAME Mix standard solution using the Supelcowax-10 column using the GC method presented in section 4.4.2.

Peak ID	Compound Name (fatty acid methyl esters)	Retention time (min)
1	C4:0 (Butyric)	5.671
2	C6:0 (Caproic)	10.658
3	C8:0 (Caprylic)	16.937
4	C10:0 (Capric)	23.124
5	C11:0 (Undecanoic)	26.042
6	C12:0 (Lauric)	28.841
7	C13:0 (Tridecanoic)	31.509
8	C14:0 (Myristic)	34.077
9	C14:1 (Myristoleic)	35.030
10	C15:0 (Pentadecanoic)	36.526
11	C15:1 (cis-10-Pentadecenoic)	37.456
12	C16:0 (Palmitic)	38.891
13	C16:1 (Palmitoleic)	39.517
14	C17:0 (Heptadecanoic)	41.139
15	C17:1 (cis-10-Heptadecenoic)	41.757
16	C18:0 (Stearic)	43.319
17, 18	C18:1n9c (Oleic) , C18:1n9t (Elaidic)	43.792
19, 20	C18:2n6c (Linoleic), C18:2n6t (Linolelaidic)	44.811
21	C18:3n6 (γ-Linolenic)	45.525
22	C18:3n3 (α-Linolenic)	46.335
23	C20:0 (Arachidic)	47.962
24	C20:1n9 (cis-11-Eicosenoic)	48.595
25	C20:2 (cis-11,14-Eicosadienoic)	50.137
26	C20:3n6 (cis-8,11,14-Eicosatrienoic)	51.083
27	C21:0 (Henicosanoic)	51.696
28	C20:3n3 (cis-11,14,17-Eicosatrienoic)	52.010
29	C20:4n6 (Arachidonic)	52.532
30	C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic)	54.752
31	C22:0 (Behenic)	55.016
32	C22:1n9 (Erucic)	56.070
33	C22:2 (cis-13,16-Docosadienoic)	58.636
34	C23:0 (Tricosanoic)	60.084
35	C24:0 (Lignoceric)	66.692
36	C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic)	68.518
37	C24:1n9 (Nervonic)	68.781

4.5.2 Characterization of Oleic Acid

For a nearly complete esterification test which could provide a characterization of the ≥90% oleic acid used in the experiments, an esterification was carried out using sulfuric acid as the catalyst. For the analysis of biodiesel produced by GC, the sample was prepared as described below:

- Measure 250 mg of oleic acid or biodiesel to a 10 mL flask.
- Add 5 mL of heptane or IS (internal standard) solution (10 mg heptadecanoate methyl ester/mL).
- Shake the solution and let it stand for 1 min.
- Dry the solution adding a micro-spatula of anhydrous sodium sulfate. Shake and let the solution stand until clarification (near 5 min).
- Inject 1 μL of the prepared solution.

4.5.3 Determination of FAME Content

For determination of FAME content of all obtained biodiesel samples (10%, 15% and 20% IL), it was used the methodology presented by European Standard EN 14103-2003 (using an internal standard - heptadecanoate methyl ester).

To calculate the FAME content, expressed as a mass content in percentage, the following equation was used:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} * \frac{C_{EI} * V_{EI}}{m} * 100\% \quad (3)$$

where:

$\sum$ **A** - total peak area from the methyl ester in C14 to that in *C*24:1;

$\mathbf{A_{EI}}$ - peak area corresponding to methyl heptadecanoate;

$\mathbf{C_{EI}}$ - concentration of the methyl heptadecanoate solution being used, mg/mL;

$\mathbf{V_{EI}}$- volume of the methyl heptadecanoate solution being used, mL;

m - mass of the sample, mg;

For calculated methyl ester area and the total FAMEs area, was used the following equation:

$$\% FAME_i = \frac{A_i}{\sum A_{FAMEs}} * 100\% \quad (4)$$

$$\% FAME_{Total} = \frac{A_{FAMEs}}{\sum A_T} * 100\% \quad (5)$$

where:

$\mathbf{A_i}$ – area of component i, %;

$\sum \mathbf{A_{FAMEs}}$ – Total area of FAMEs, %;

$\mathbf{A_T}$ – Total area of peaks, %.

4.6 Ionic Liquid Analysis with UV Spectrophotometer

For this analysis the VARIAN Cary 50 UV-Vis Spectrophotometer was used (see Figure 20).

Preparation the sample:

- Measure 0.05 mL of Ionic Liquid to a 100 mL flask.
- Add 100 mL of methanol (MeOH).
- Shake the solution manually.
- Then measure 0.5 mL of the solution to a 50 mL flask.
- Add 50 mL of MeOH.
- Analyse the solution by UV.

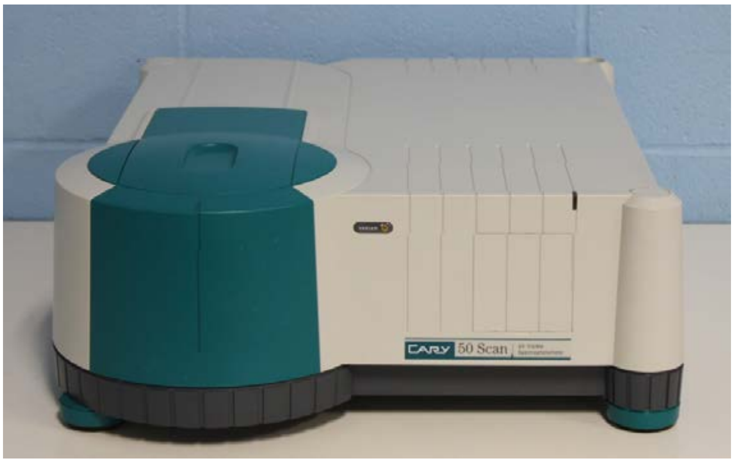


Figure 20. VARIAN Cary 50 UV-Vis Spectrophotometer.

4.7 Ionic Liquid Analysis with Fourier Transform Infrared Spectroscopy (FTIR)

Mid-Infrared (IR) spectroscopy is a highly reliable and well recognized fingerprinting method. By this analysis more substances can be characterized, identified and also quantified. By IR spectroscopy spectra from a very wide range of solids, liquids and gases can be obtained. For ILs characterization a FTIR ABB MB300 spectrometer was used (see Figure 21).

Figure 21. FTIR ABB MB300 spectrometer.

As with all FT-IR measurements, an infrared background is collected, in this case, from the clean ATR crystal. The crystals are usually cleaned by using a solvent soaked piece of tissue. Typically water, methanol or isopropanol are used to clean ATR crystals. The ATR crystal must be checked for contamination and carry over before sample presentation, this is true for all liquids. After the crystal has been cleaned and an infrared background has been collected, the liquid is simply poured onto the crystal. The whole crystal must be covered if performing a quantitative or qualitative analysis. The crystal is recessed into the metal plate to retain the sample (see Figure 22).

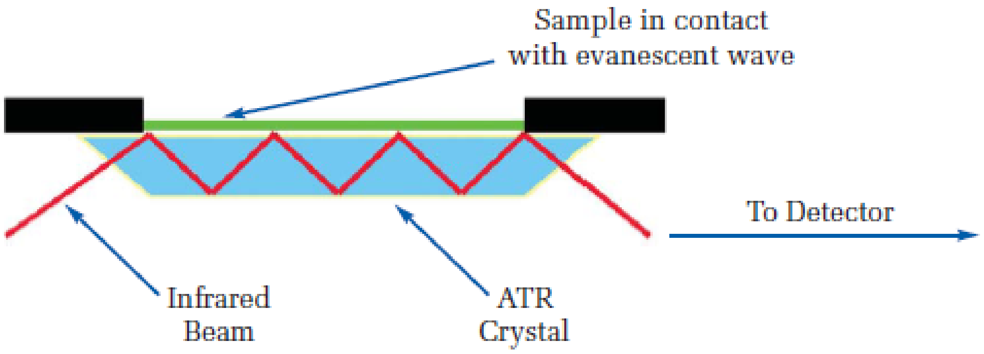


Figure 22. A multiple reflection ATR system.

5 Results and Discussion

5.1 The Selection of the Ionic Liquid

For the selection of the best ionic liquid for the esterification reaction, between oleic acid and methanol several experiments were made using different IL´s as catalysts. The parameters for each reaction and the conversion are presented in Table 9, for the IL´s used and also for sulfuric acid. Amount of sulfuric acid was a 10%.

For the experiments done with ionic liquids as catalysts the molar ratio between oleic acid and methanol was 1/10 and the quantity of IL was 10%, 15%, 20 % of oleic acid. In the first experiment 1-butyl-3-methylimidazolium hydrogen sulfate was used as catalyst. And the reaction time was 2 hours. After the reaction, it was necessary to wait 7 days for the separation of phases. After that time some water was, added to the mixture and then this mixture was left to rest for 2 days and after separation of phases occurred. The yield of this reaction was a 57.7 %. The second experiment was done in the same way, but this time 1-butyl-3-methylimidazolium methyl sulfate was used as catalyst and reaction time was 4 hours. With this IL the separation of phases occurred after 2 days. And the conversion was a 76.4 %. For the experiment 3 the catalyst used was 1-methylimidazolium hydrogen sulfate. The reaction time was 6 hours. Right after reaction finished, the phases separated. Next day it was possible to separate the phases and measure the respective masses. The conversion was 88.5 %.

Table 9. Biodiesel production yield using different ionic liquids in different time (10% IL)

Catalyst	m Ionic Liquid (g)	m Oleic Acid (g)	V MeOH (ml)	t (h)	T(°C)	Conversion %
[BMIM][HSO_4]	0.5714	5.6608	8.1	6	90	76.6
[BMIM][$MeSO_4$]	0.5654	5.6235	8.1	4	90	76.4
[MIM][HSO_4]	0.5624	5.6075	8.1	6	90	88.5
$C_9H_{18}N_2O_3S$	0.5617	5.6365	8.1	6	90	18.4
$C_{14}H_{33}NO_4S$	0.5682	5.6802	8.1	6	90	15.4

The reaction using 1-butyl-3-methylimidazolium methanesulfanate as catalyst took 6 hours. In this case the phases took 2 weeks to separate. It was verified that the acidity of organic phase was a higher compared to the other experiments and the conversion was only 18.4 %. The next experiment was done using tributylmethylammonium methyl sulphate as catalyst. The conditions used to the reaction were the same as before. In this case the phases separated after one week. But yield was very low, only 15.4 %. The esterification reaction was also done using sulphuric acid as catalyst, to have a “complete” esterification. The obtained yield was 99.0 %. After these first experiments we decided to continue the work using [BMIM][HSO_4] as catalyst: because, this IL is one of the best ILs which have the higher yield and with this ILs have a study which continue in this work [*Alimova, 2016*]. Also, after esterification, a separation phase was faster than using other ILs.

Several experiments were made using [BMIM][HSO_4] as catalyst and the percentage of IL was varied (10%, 15% and 20%). Acidity of oleic acid was a 183.7482, reaction time 6 h, reaction temperature 90^{o}C. In Table 10 presented the results.

Table 10. Effect of quantity of [BMIM][HSO_4] on production conversions

Quantity of ILs (%)	m Ionic Liquid (g)	m Oleic Acid (g)	V MeOH (ml)	Conversion %
10	1.1560	11.3239	16.20	76.6
15	1.7383	11.3474	16.23	83.3
20	2.2312	11.2969	16.23	84.9

The conversions obtained for these experiments are in the range 76.6% -79.7% %. In Figure 23 is presented a picture of the biodiesel obtained in these reactions. The biodiesel has a yellow color.

Figure 23. Biodiesel which we got from this reaction

5.2 Internal Standard characterization

The quantification of the ester and linoleic acid methyl ester content in biodiesel samples can be performed using the European Standard EN 14103 (April 2003). The methodology proposed implies the use of methyl heptadecanoate (minimum purity of 99%) as internal standard for GC analysis (10 mg/mL in heptane). However, since the solid available for this work has a purity of 97.5%, it was decided to study if this standard can add some impurities to biodiesel samples analysis.

The GC chromatogram obtained for the methyl heptadecanoate solution (10 mg/mL) is presented in Figure 24.

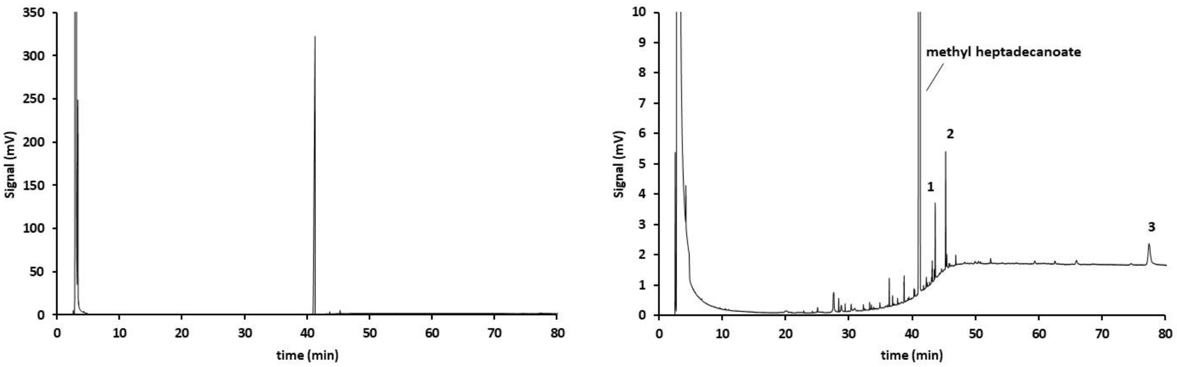


Figure 24. GC chromatogram obtained for the methyl heptadecanoate solution (10 mg/mL). Both figures represent the same chromatogram (right figure used to visual identify the main peaks in baseline).

From the right amplified chromatogram we can see three main impurities (peak area above 10000) present in the standard solution. With this analysis it was possible to obtain the purity for the internal standard solution of 99.2% (higher than the value indicated in the label of the reagent flask, ≥97.5%). This value was obtained by the ratio of the area of methyl heptadecanoate and the total area of all peaks having a minimum area of integration of 10000. This integration parameter as well as a signal to noise ratio of 1:5 was used for all the biodiesel samples analysis, presented in the following sections. It was decided not to consider all these impurities added by the internal standard in the quantification process for all the samples obtained in the recovery studies. The retention times of these non- identified (NI) peaks are 43.6, 45.3 and 77.4 min, for 1, 2 and 3, respectively.

5.2.1 Complete esterification of Oleic Acid using sulfuric acid

Other experimental task was the characterization of the oleic acid used as organic raw material for the esterification reaction to produce biodiesel. This reagent was available with a purity of ≥90% and it was decided to measure the maximum quantity of methyl ester obtained by a “complete” esterification using sulfuric acid as catalyst.

The GC analysis of biodiesel sample obtained by esterification with sulfuric acid and analyzed using the internal standard methodology is presented in Figure 25.

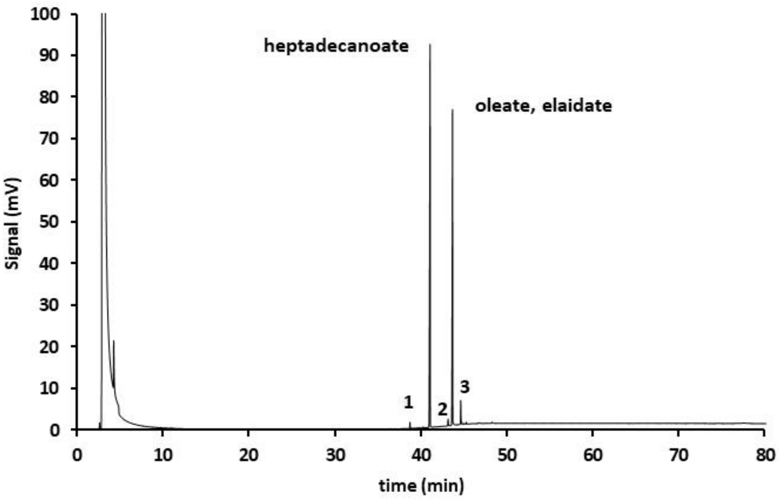


Figure 25. GC chromatogram obtained for the biodiesel sample obtained from esterification using sulfuric acid and with the addition of the internal standard.

The analysis of this chromatogram shows two main peaks: first the peak of the methyl ester of heptadecanoate, used as internal standard, and then the peak of oleate (from oleic acid) and elaidate (from elaidic acid) methyl esters that co-elute. There are also three small peaks that represent the esterification of other fatty acids present in the original oleic acid reagent: (from palmitic, stearic and linoleic acids, respectively). The experimental concentration of oleic acid methyl ester was 96.6% (g oleic methyl ester /g total fatty acid methyl esters).

5.3 Characterization of biodiesel samples using different amounts of ionic liquid

To study of the effect of the recovery of the [BMIM][HSO_4] in the performance of the next esterification step, 3 esterification reactions (With 10%, 15% and 20% amounts of ILs) were carried out followed by 4 (10% amount of IL) and 5 (15%, 20% amounts of IL) recovery steps. For the first recovery only 4 reactions, because after fourth recovery of IL mass was very small. The yields obtained for the reactions carried out with higher amounts of IL (15 wt% and 20 wt%) are higher than those obtained for the reactions with 10 wt% of IL. In Table 11 are presented the obtained results of conversion for these reactions.

Table 11. Number of runs (recovery) ILs 10%, 15%, 20% and reaction conversions.

Number of runs	**Conversion %**					
	ILs 10 wt %	**Name**	**ILs 15 wt %**	**Name**	**ILs 20 wt %**	**Name**
1	76.6	REC 10.1	83.3	REC 15.1	84.9	REC 20.1
2	73.7	REC 10.2	79.9	REC 15.2	81.5	REC 20.2
3	67.4	REC 10.3	77.0	REC 15.3	81.8	REC 20.3
4	58.3	REC 10.4	79.1	REC 15.4	80.7	REC 20.4
5	---	---	75.3	REC 15.5	77.1	REC 20.5

In Figure 26 is presented biodiesel conversion dependencies from amount of catalyst and recovery runs. It is possible to verify that when amount of ILs increase also increase biodiesel conversion.

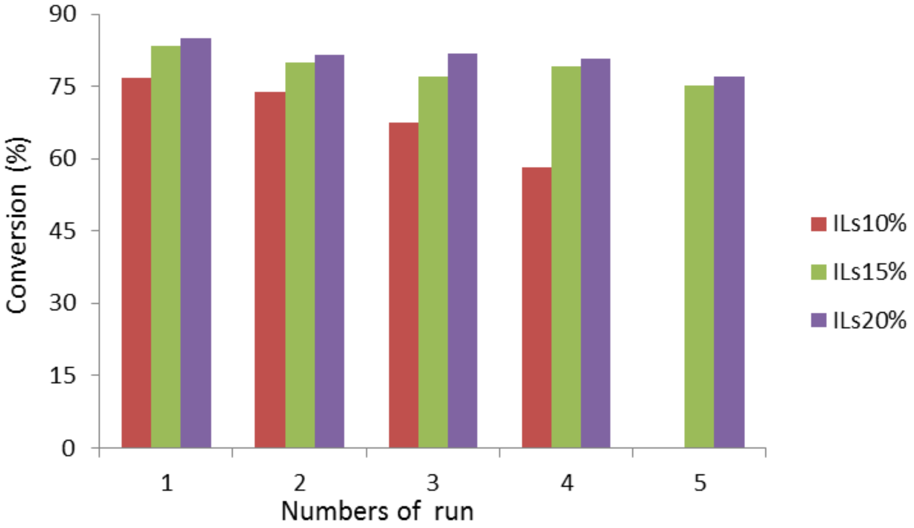


Figure 26. Reaction conversions dependency from amount catalyst and number of runs (recovery) ILs 10%, 15%, 20%.

For doing recovery, the flask containing the water phase was weighted, after added water phase. After recovery was measured the flask and ILs together. After four successive reactions mass of IL decreased about 60.8 % (reaction with ILs 10%), in reaction with 20%, 15% IL after 5 runs the mass of IL decreased about 28 % and in reaction with 20% of IL, the IL mass decreased 23.8 %. All results are presented in Table 12.

Table 12. ILs mass after from recovery runs

Number of runs	**IL mass (g) (10 wt% IL)**	**IL mass (g) (15 wt% IL)**	**IL mass (g) (20 wt% IL)**
1	1.156	1.7383	2.2312
2	1.156*	1.7383*	2.2312*
3	0.804	1.7383*	2.2312*
4	0.453	1.4291	1.8136
5	---	1.2500	1.6690

*After recovery mass of IL was a higher and was considered that all initial mass in recovery sample.

In Figure 27 is shown ILs mass (g) dependency from number of runs (recovery) for IL 10%, 15%, 20%. When numbers of run increases, mass of ILs decreases.

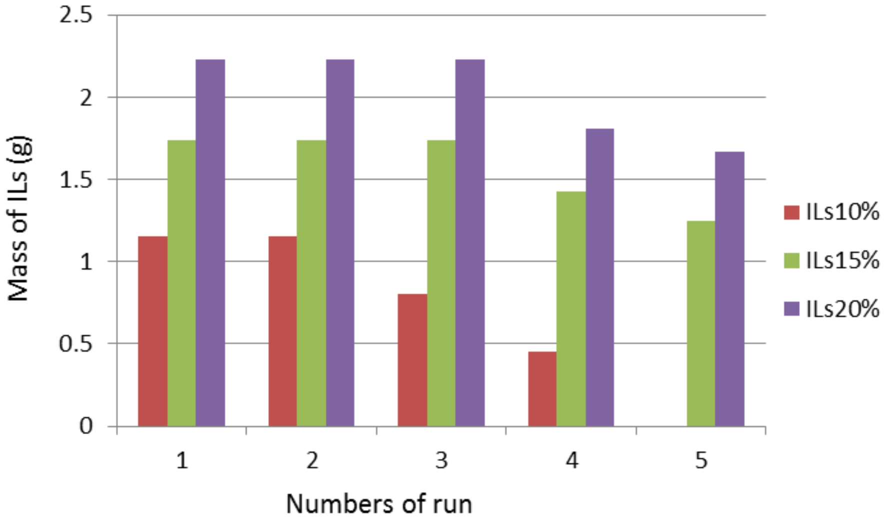


Figure 27. ILs mass (g) dependency from numbers of run (recovery) ILs 10%, 15%, 20%.

5.3.1 Ratio of Ionic Liquid to Oleic Acid of 10%

The GC chromatograms for the analysis of all the biodiesel obtained using a 10 wt% of ionic liquid is presented in Figure 28.

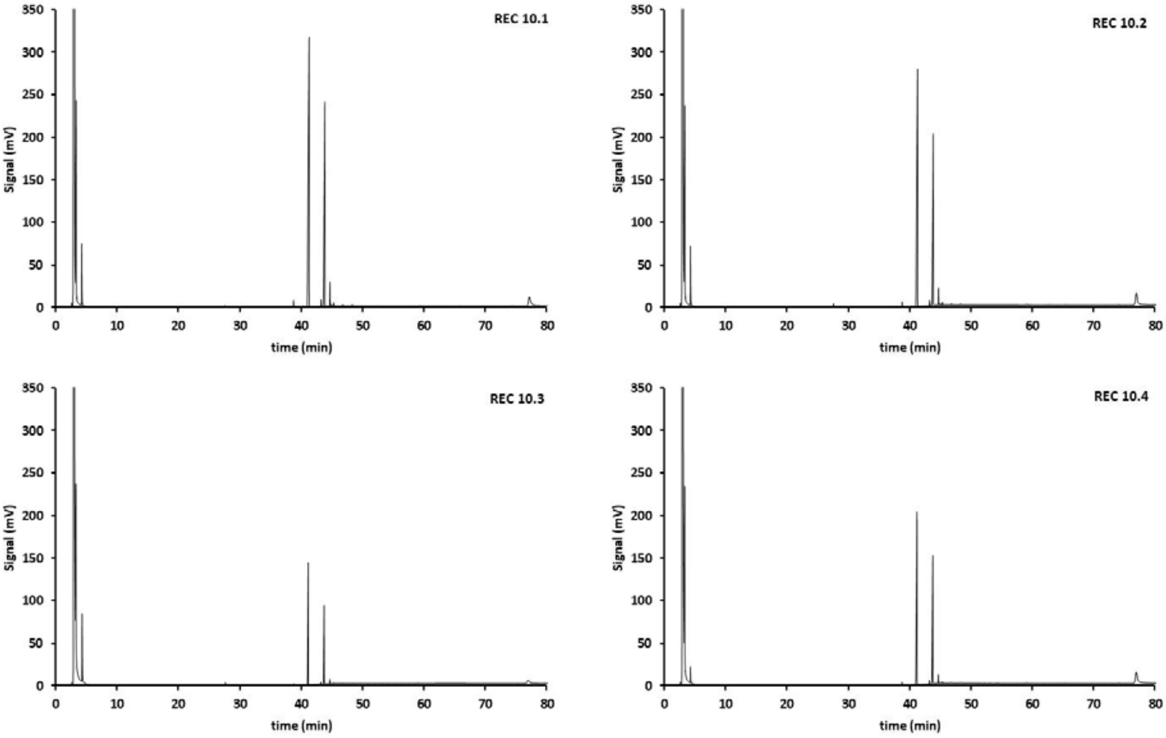


Figure 28. GC chromatograms obtained for the biodiesel samples obtained for 10% IL, from esterification after 4 recovery steps (REC 10.1 to 10.4).

The experimental concentration of FAME content in these samples was obtained using the same methodology explained before (EN 14103-2003). The experimental concentrations (g FAMEs/g biodiesel) values are 61.2%, 49.4%, 43.5% and 56.2%. Concentration of REC 10.4 was a higher then Rec 10.2 and Rec 10.3: probably it was experimental error.

5.3.2 Ratio of Ionic Liquid to Oleic Acid of 15%

The GC chromatograms for the analysis of all the recovered biodiesel samples obtained using a 15% of ionic liquid are presented in Figure 29.

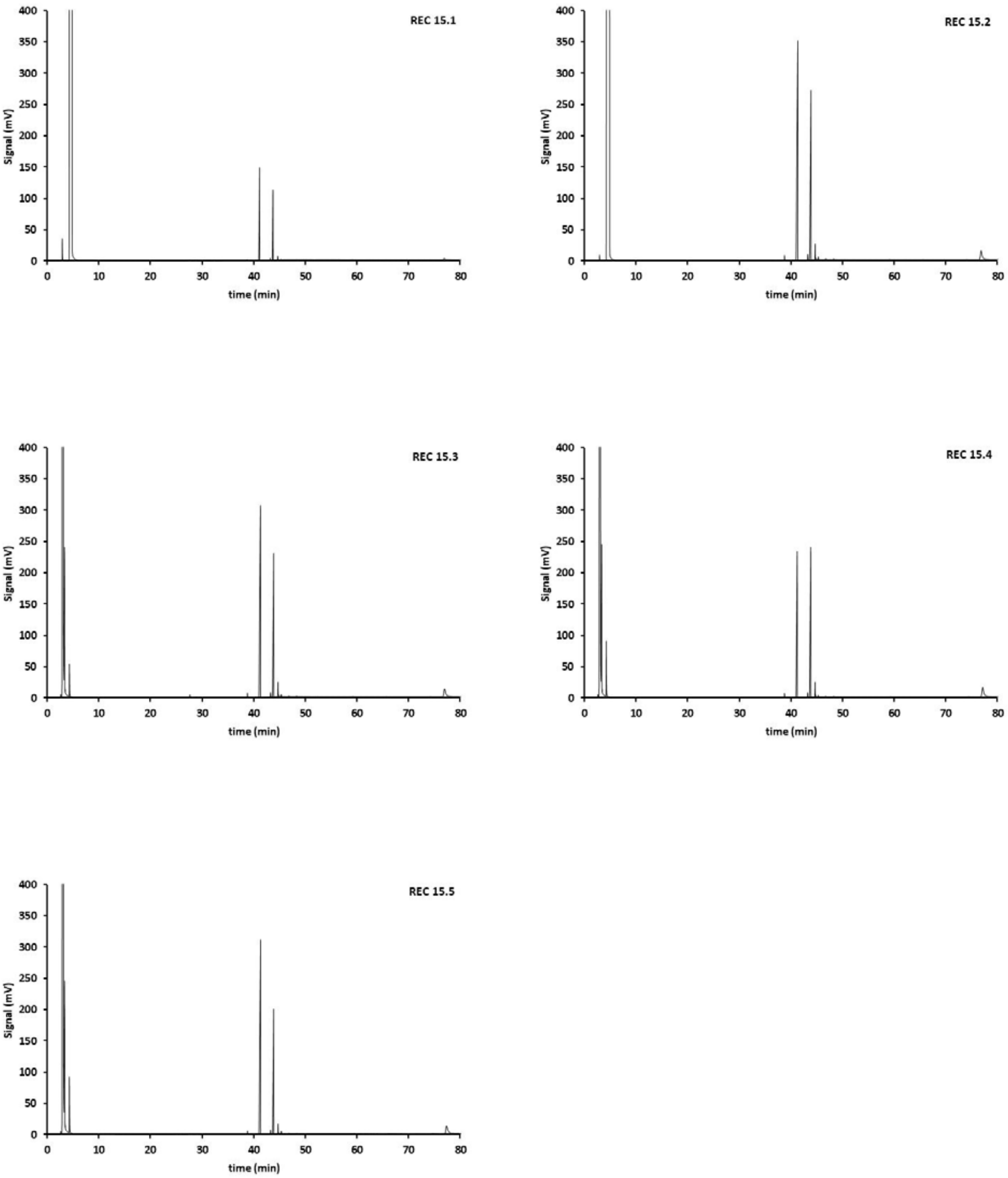


Figure 29. GC chromatograms obtained for the biodiesel samples obtained for 15% IL, from esterification after 4 recovery steps (REC 15.1 to 15.5).

The experimental concentration of FAME content in these samples was obtained using the same methodology explained before (EN 14103-2003). The experimental concentrations (g FAMEs/g biodiesel) values are 63.1%, 59.0%, 55.0%, 95.6% and 44.5%. The outlier value of 95.6% (REC 15.4) it was considered has being due to an experimental error.

5.3.3 Ratio of Ionic Liquid to Oleic Acid of 20%

The GC chromatograms for the analysis of all the recovered biodiesel samples obtained using a 20% of ionic liquid are presented in Figure 30.

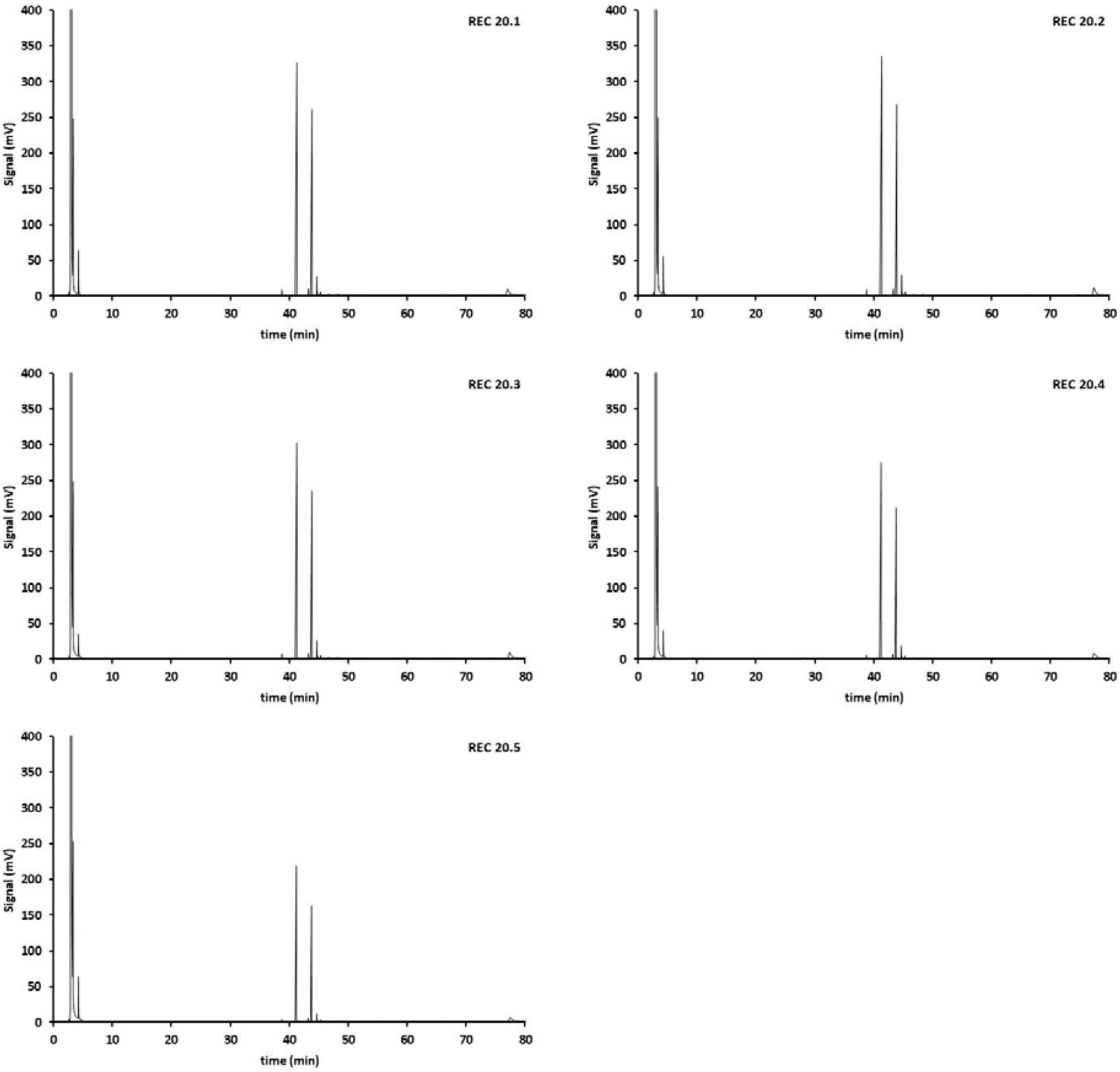


Figure 30. GC chromatograms obtained for the biodiesel samples obtained for 20% IL, from esterification after 4 recovery steps (REC 20.1 to 20.5).

The experimental concentration of FAME content in these samples was obtained using the same methodology explained before (EN 14103-2003). The experimental concentrations (g FAMEs/g biodiesel) values are 64.7%, 60.5%, 62.6%, 59.9% and 56.5%.

5.4 ILs analysis by UV-VIS

Ionic liquids can be transparent in the near-ultraviolet and visible spectral regions, in contrast to many other polar organic solvents. This makes that ionic liquids are very interesting solvents for spectroscopic measurements on dissolved metal salts and metal complexes. For the quality control of ionic liquids, UV/VIS spectrophotometry was applied. It is an efficient method [*Nockemann- 2005*]. The effect of the recovery steps in the quality of the ionic liquid was studied by UV-VIS spectroscopy. The spectrum of original IL and the ILs recovered after the final esterification reaction, for each %IL is presented in Figure 31. The original ILs has a yellow colour, but the recovery ILs sample has a little bit dark colour. In Figure 31, the absorption spectra of samples of the ionic liquid [BMIM][HSO_4] are shown. The spectra were recorded in a 1 cm quartz cell. The absorption spectrum of the original ionic liquid (red, solid line) shows an absorption maximum around 260 nm.

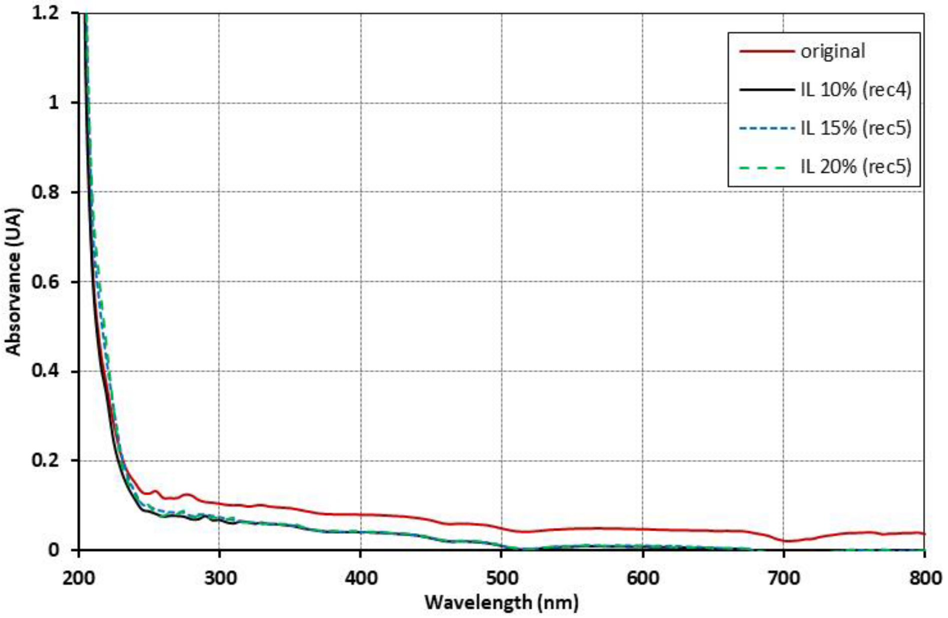


Figure 31. UV-Vis spectrum obtained for original and the recovered ILs obtained for different amount of ILs (10, 15 and 20%).

The original ionic liquid [BMIM][HSO_4] 0.11 absorbance threshold shifts for the original ILs sample from 200 nm to about 260 nm, the spectra of the recovered not differ from each other's and show absorption bands at for ILs (REC20) 200 nm to 250 nm ,for ILs (REC15) 200 nm to 264, for ILs (REC10) 200nm to about 255. Spectroscopic results prove the [BMIM][HSO_4] after recovery retained stable catalytic performance.

5.5 ILs analysis by FTIR

The effect of the recovery steps in the quality of the ionic liquid was studied by Fourier Transform Infra-Red (FTIR) spectroscopy.

The molecular formula for the ionic liquid, 1-Butyl-3-methylimidazolium hydrogen sulfate is [BMIM][HSO_4]. Figure 32 shows the structural formula of the sample.

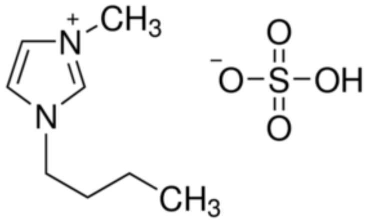


Figure 32. Formula 1-Butyl-3-methylimidazolium hydrogen sulfate.

The spectrum of original IL, methanol and the ILs recovered after the final esterification reaction, for each %IL is presented in Figures 33 to 36. It is commonly acknowledged that the characteristic absorption peaks of [BMIM][HSO_4] appear at 3148 cm^{-1} , 3101 cm^{-1} , 2962 cm^{-1} , 2869 cm^{-1} , 1566 cm^{-1} , 1464 cm^{-1} , 1220 cm^{-1} , 1160 cm^{-1} , 1030 cm^{-1} , 835 cm^{-1} , 755 cm^{-1}. And for methanol 555 cm^{-1}.

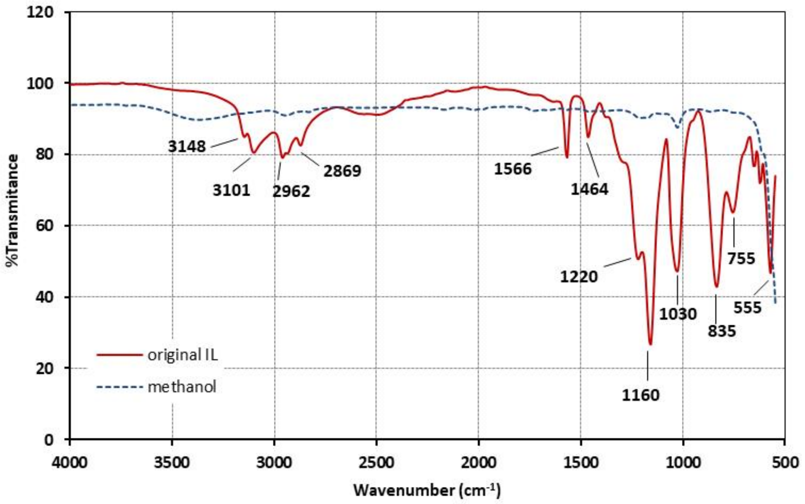


Figure 33. FTIR spectrum obtained for original IL and methanol.

Table 13 is based on the results presented in Figure 33. This table presents the functional groups that can be identified in the ionic liquid according to the peaks shown in the spectrum.

Table 13. Functional group of the components of original IL [*Colthup et al., 2009*]

Wavelength cm^{-1}	Functional group	Molecular motion
755	1. Aromatics	1. C-H bend (meta) ~690
835	1. alkenes 2. sulfones 3. amines	1. C-H bend (disubstituted -1,1) ~890 2. S-O bend 900-800 3.NO_2 bend 900-800
1030, 1160,1200	1. ketones 2. amines 3. sulfones	1. C-C stretch 1300-1100 2. C-N stretch (alkyl) 1200-1025 3. SO_3 symmetric deformation 1100-1000
1160	1. alcohols 2. ketones	1. C-O stretch 1260-1000 2. C-C stretch 1300-1100
1464	1.alkenes 2. sulfones	1. CH_2 bend ~1465 2. SO_2 asymmetric stretch 1450-1100
1566	1.amines	1. N-H bend 1640-1500
2869, 2962, 3101, 3148	1.carboxylic acid 2. alkenes	1. O-H stretch 3400-2400 2. CH_2 bend 3250-2700

Figure 34 of ionic liquid REC4 presented peaks of SO_3 at 1013 and 1046 cm^{-1}, which correspond to symmetric stretching. The strong adsorption peaks at 3107 cm^{-1}, 1644, 2962 cm^{-1} were assigned to the C–H, C = C ring stretching vibration of benzylamine.

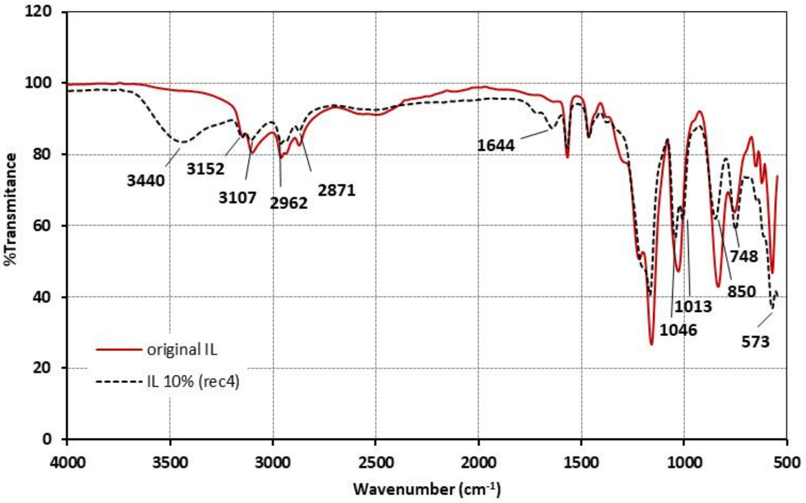


Figure 34. FTIR spectrum obtained for original IL 10% (REC4).

The bands at 1013, 1046 cm^{-1} were assigned to the S = O asymmetric and symmetric stretching vibrations of the –SO_3H group. Table 14 presents the functional groups of ionic liquid according the peak from Figure 34.

Table 14. Functional group of the components of IL 10% (REC4) [*Colthup et al., 2009*]

Wavelength cm^{-1}	Functional group	Molecular motion
748	1. Aromatics	1. C-H bend (meta) ~690
850	1. alkenes 2. sulfones 3. amines	1. C-H bend (disubstituted -1,1) ~890 2. S-O bend 900-800 3.NO_2 bend 900-800
1013,1046	1. ketones 2. amines 3. sulfones	1. C-C stretch 1300-1100 2. C-N stretch (alkyl) 1200-1025 3. SO_3 symmetric deformation 1100-1000
1644	1.amines	1. N-H bend 1640-1500
2871, 2962 3107, 3152, 3440	1.carboxylic acid 2. alkenes	1. O-H stretch 3400-2400 2. CH_2 bend 3250-2700

In Figure 35 we can see that there are a new peaks present at 3102 cm^{-1} and 2856 cm^{-1}, due to the OH of an alcohol or carboxylic acid, in our case could be due to a contamination of biodiesel sample with methanol. It is possible to see also new peaks at 1738 cm^{-1} and 1712 cm^{-1} can be alkenes group.

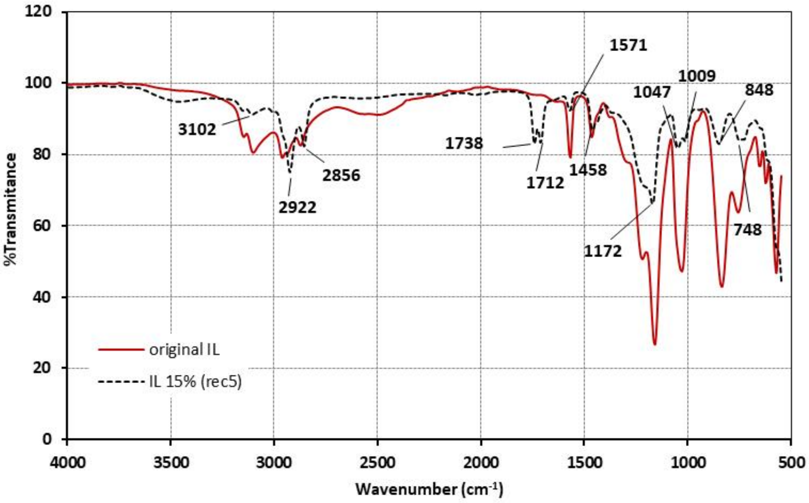


Figure 35. FTIR spectrum obtained for original IL 15% (REC5).

All characteristic absorption peaks of IL 15 % (REC 5) appear at 3102 cm^{-1}, 2922 cm^{-1}, 2856 cm^{-1}, 1738 cm^{-1}, 1712 cm^{-1}, 1571 cm^{-1}, 1458 cm^{-1}, 1047 cm^{-1}, 1009 cm^{-1}, 848 cm^{-1}, 748 cm^{-1} . All functional groups of the components of IL 15 % (REC 5) are shown in Table 15.

Table 15. Functional groups of the components of IL 15% (REC5) [*Colthup et al., 2009*]

Wavelength cm^{-1}	Functional group	Molecular motion
748	1. Aromatics	1. C-H bend (meta) ~690
848	1. alkenes 2. sulfones 3. amines	1. C-H bend (disubstituted -1,1) ~890 2. S-O bend 900-800 3.NO_2 bend 900-800
1009, 1047, 1172,	1. ketones 2. amines 3. sulfones	1. C-C stretch 1300-1100 2. C-N stretch (alkyl) 1200-1025 3. SO_3 symmetric deformation 1100-1000
1160	1. alcohols 2. ketones	1. C-O stretch 1260-1000 2. C-C stretch 1300-1100
1458	1.alkenes 2. sulfones	1. CH_2 bend ~1465 2. SO_2 asymmetric stretch 1450-1100
1738, 1712	1.alkenes	1.CH_2 medium 1850-1750
2856, 2922, 3102	1.carboxylic acid 2. alkenes	1. O-H stretch 3400-2400 2. CH_2 bend 3250-2700

The characteristic absorption peaks of IL 20 % (REC 5) appear at 3450 cm^{-1}, 3100 cm^{-1} , 2960 cm^{-1}, 2870 cm^{-1}, 1568 cm^{-1}, 1466 cm^{-1}, 1215 cm^{-1}, 1163 cm^{-1}, 1038 cm^{-1}, 1008 cm^{-1}. The spectra showed a new peak present at 3440 cm^{-1}, due to the OH of an alcohol or carboxylic acid.

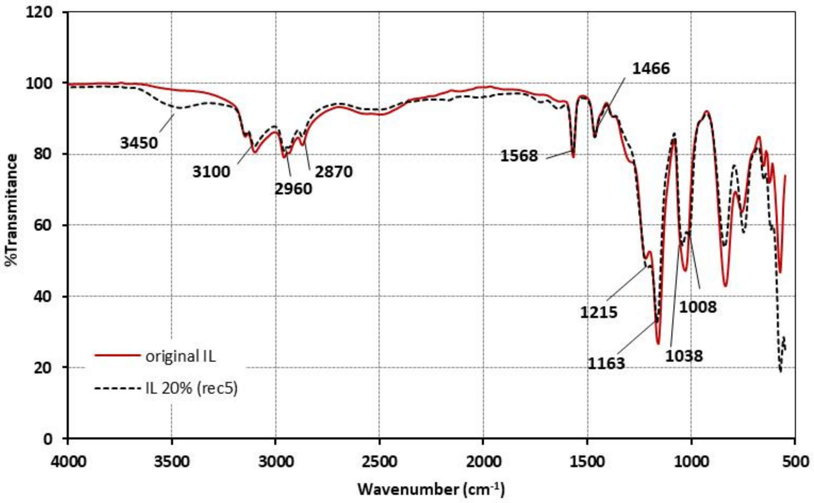


Figure 36. FTIR spectrum obtained for original IL 20% (REC5).

Figure 36 also shows the strong peak 1163 cm $^{-1}$, the same peak we can see in Original IL spectra. It is can be alcohols or ketones. In Table 16 shown functional group of the components of IL 20% (REC5).

Table 16. Functional group of the components of IL 20% (REC5) [*Colthup et al., 2009*].

Wavelength cm^{-1}	Functional group	Molecular motion
1008, 1038, 1163, 1215	1. alcohols 2. ketones	1. C-O stretch 1260-1000 2. C-C stretch 1300-1100
1466	1.alkenes 2. sulfones	1. CH_2 bend ~1465 2. SO_2 asymmetric stretch 1450-1100
1568	1.amines	1. N-H bend 1640-1500
2870, 2960, 3100, 3450	1.carboxylic acid 2. alkenes	1. O-H stretch 3400-2400 2. CH_2 bend 3250-2700

6. Conclusions and Future work

The effect of different reaction for biodiesel production was studied using different ionic liquid as a catalyst. The study of the esterification of oleic acid with ionic liquids was carried out for obtaining high yield biodiesel production. For analyzing the biodiesel samples was used a GC.

In this dissertation different esterification reactions were carried out with different kind of ILs. The conversion varied between an 18 -88 %. For the study we selected [BMIM] [HSO_4] ionic liquid. The reaction yield was found to be 76.6% to 10% IL, 83.3% to 15% IL and 84.8% to 20% IL. These yields decreased to 58.2% (10% IL) with 4 cycles of recycling, 75.2% (15% IL) with 5 cycles of recycling and 77.1% (20% IL) with 5 cycles of recycling. In this work the FAME content was calculated: values of around 50-60% of FAMEs / g biodiesel sample. Another 40-50% could be in the organic phase (as acids) or in the aqueous phase.

For analyzing the ILs was used UV-VIS and FTIR. And found that it retained stable catalytic performance after recovery.

Future work

In this thesis work, there are some further important researches that need to study. In this dissertation esterification reaction, were carried out for biodiesel production, using methanol and oleic acid and ILs as a catalyst. Though, in the future experiments will be testing other acids for biodiesel production.

The IL ([BMIM] [HSO_4]) recovery was. Catalyst recovery was a 5 time (5 recycling). However, in the future experiments will be for improving conditions of recovery: heating time and temperature. Improve the recovery runs to increase 6-8 times. And also in the future experiments will be testing other ILs for recovery.

In this work used GC analysis for biodiesel sample, and UV-VIS and FTIR for ILs analysis. But in future have to be doing the FTIR analysis for oleic acid. And use more methods for analysis.

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Appendix

Appendix A Titration Values

Appendix A1 different Ionic liquids

Table A1. Titration data and obtained acid number and biodiesel yield

ILs wt 10%, AO/MeOH 1/10	Initial acidity of AO	Acidity mg KOH/g	Conversion %	Concentration of KOH/MeOH solution
[BMIM][HSO_4]	183.7482	77.6827	57.7233	0.07859
[BMIM][$MeSO_4$]	183.7482	42.3879	79.4544	0.07859
[MIM][HSO_4]	183.7482	21.1044	88.5145	0.07859
$C_9H_{18}N_2O_3S$	183.7482	149.9827	18.376	0.07859
$C_{14}H_{33}NO_4S$	183.7482	155.4739	15.3875	0.07859

Appendix A2 [BMIM][HSO_4] Ionic liquids

Table A2. Titration data and obtained acid number and biodiesel yield

ILs wt 10%, AO/MeOH 1/10	Initial acidity of AO	Acidity (mg KOH/biodiesel)	Conversion %	Concentration of KOH/MeOH solution
[BMIM][HSO_4]	183.7482	41.0333	79.68	0.07859
[BMIM][HSO_4]	183.7482	39.952	77.66	0.07859
[BMIM][HSO_4]	183.7482	42.9217	76.64	0.07859
[BMIM][HSO_4]	183.7482	48.2603	78.25	0.07859

Appendix A3 Ionic liquids recovery, Ionic Liquids amount

Table A3.1. Titration data and obtained acid number and biodiesel yield

Numbers of run	ILs wt 10%, AO/MeOH 1/10	Initial acidity of AO	Acidity (mg KOH/biodiesel)	Conversion %	Concentration of KOH/MeOH solution
1	[BMIM][HSO_4]	183.7482	42.9217	76.64	0.07859
2	[BMIM][HSO_4]	183.7482	48.2603	73.73	0.07859
3	[BMIM][HSO_4]	183.7482	59.8899	67.4	0.07859
4	[BMIM][HSO_4]	183.7482	76.6264	58.29	0.07859

Table A3.2. Titration data and obtained acid number and biodiesel yield

Numbers of run	ILs wt 15%, AO/MeOH 1/10	Initial acidity of AO	Acidity (mg KOH/biodiesel)	Conversion %	Concentration of KOH/MeOH solution
1	[BMIM][HSO_4]	183.7482	30.6249	83.3332	0.07436
2	[BMIM][HSO_4]	183.7482	36.9076	79.914	0.07436
3	[BMIM][HSO_4]	183.7482	42.2800	76.99	0.07436
4	[BMIM][HSO_4]	183.7482			0.07436

Table A3.3. Titration data and obtained acid number and biodiesel yield

Numbers of run	ILs wt 20%, AO/MeOH 1/10	Initial acidity of AO	Acidity (mg KOH/biodiesel)	Conversion %	Concentration of KOH/MeOH solution
1	[BMIM][HSO_4]	183.7482	27.7729	84.8856	0.07436
2	[BMIM][HSO_4]	183.7482	33.9143	81.5431	0.07436
3	[BMIM][HSO_4]	183.7482	33.4359	81.8034	0.07436
4	[BMIM][HSO_4]	183.7482			0.07436