# Production of Biodiesel through Esterification Catalysed by Ionic Liquids

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# Abstract

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. Currently, most biodiesel is made from oils, methanol, and an alkaline catalyst. Conventional catalysts is commonly used for catalyzing esterification of fatty acid to produce biodiesel. However, a better and greener method was found. An ionic liquid (IL) is a molten salt consisting of a cation and an anion, with low melting temperature. It offers a better solution than sulfuric acid, because it can be recycled and reused in subsequent runs after recovery steps. In this study, a Brønsted acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][$HSO_4$]) was used as a catalyst in the esterification of oleic acid with methanol into biodiesel.

The effect of different operation parameters such as methanol to oil molar ratio, amount of catalyst, reaction temperature, and reaction time were tested. The optimum conditions for esterification of oleic acid were identified as oleic acid/methanol molar ratio of 1/10, amount of catalyst 10 wt%, reaction time of 4 h, and reaction temperature of 90$^{o}$C. FAME content of produced biodiesel was analyzed and confirmed using GC chromatography.



**Keywords**: biodiesel, optimization, esterification, ionic liquid.

## Resumo

O Biodiesel é uma alternativa interessante aos combustíveis fósseis, sendo produzido a partir de óleos vegetais e/ou gorduras animais. Atualmente, a maior parte do biodiesel é produzido utilizando óleos, metanol e um catalisador alcalino. Os catalisadores tradicionais são normalmente usados em catálise ácida de ácidos gordos para produzir biodiesel. Contudo, um método alternativo e mais "amigo" do ambiente tem sido recentemente, bastante estudado. Os líquidos iónicos são sais fundidos/líquidos constituídos por um catião e por um anião com pontos de fusão reduzidos. Estes compostos são uma solução melhor quando comparados com o ácido sulfúrico, podendo ser reciclados e reutilizados. Neste trabalho utilizam-se como catalisadores, ácido sulfúrico, e um líquido iónico: o 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][$HSO_4$]). Sendo ambos utilizados como catalisadores na esterificação do ácido oleico com metanol para produzir biodiesel.

O principal objetivo deste trabalho consistiu em estudar a influência de alguns parâmetros de operação na produção de biodiesel, como seja a razão molar metanol/ácido oleico, a quantidade de catalisador, a temperatura da reação e o tempo de reação. O estudo realizado permitiu identificar as condições ótimas para cada um destes parâmetros: razão molar ácido oleico/metanol de 1/10, quantidade de catalisador de 10% em massa, tempo de reação de 4 h e temperatura de reação de 90$^{o}$C. O conteúdo em ésteres metílicos de ácidos gordos (FAMEs) do biodiesel produzido foi igualmente caracterizado por cromatografia gasosa quer qualitativamente quer quantitativamente.



**Palavras-Chave**: biodiesel, otimização, esterificação, líquidos iónicos

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# 1 Introduction

In recent decades, there is a growing interest in the development of alternative technologies to the oil economy, based on so called renewable energy sources. One of the possible solutions is a usable biofuel 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 put problems in the classic process of production of biodiesel 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.

Biodiesel is an environmentally friendly alternative diesel fuel consisting of the alkyl monoesters of fatty acids from vegetable oils and animal fats [1]. Biodiesel is a non-toxic, biodegradable, renewable fuel that can be produced from a range of organic and renewable raw material including new or waste vegetable oils and animal fats. Biodiesel 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. In addition, biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability [2]. There are different raw materials for biodiesel production. Currently, edible oils are the main resources for world biodiesel production. However, there are many reasons for not using it. Therefore, 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. The main attention is paid to optimization of reaction parameters.

## Background and Motivation

Renewable energy has attracted more attention recently. Biodiesel, one of the renewable energy, has been recognized as an interesting fuel that substituted diesel oil produced from petroleum.

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 put problems in the classic process of production of biodiesel 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. Therefore, 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; transesterification reactions of mixtures of triglycerides with high levels of FFA's; and transesterification reactions of high acidity waste cooking oils.

## 1.1 Main Objectives

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The main objective of this work was to determine the influence of the operating conditions on the kinetics and on the equilibrium of the esterification of oleic acid with methanol. The experimental work included the optimization of the main reaction parameters (temperature, time, methanol/oleic acid ratio, amount of ionic liquid). In the following work 1-butyl-3-methylimidazolium hydrogen sulfate ionic liquid was tested in the synthesis of biodiesel from esterification oleic acid with methanol. Optimization yield of conversion was determined by volumetric titration and confirmed by Gas Chromatography analysis.

## 1.2 Outline of the report

The first chapter of this thesis work presents an Introduction to biodiesel as a renewable source. Chapter 2 and 3 is the literature review with information about biodiesel properties and production and types of ionic liquids. Chapter 4 describes the methodology and details of the experimental work. Chapter 5 presents and discusses the obtained results, and all work concludes in Chapter 6 with suggestions for future work.

## 2. Biodiesel as a renewable energy source

Biodiesel is a renewable, biodegradable, non-toxic, sulfur-free, and environmentally clean alternative diesel fuel. Biodiesel is composed by fatty acid methyl (or ethyl) esters, produced from renewable resources, such as vegetable oils, animal fats, and waste restaurant greases. 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 [1]. Biodiesel fuel in comparison with diesel fuel has advantages in terms of sulfur content, flash point, aromatic content and biodegradability. Also biodiesel has lower emissions than petroleum diesel 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 [2].

## 2.1 Physicochemical properties

Biodiesel is a liquid biofuel, 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.

Table 1. Biodiesel properties [3]

| | |
|---|---|
| Kinematic viscosity at 40°C, $mm^2/s$ | 4.0 to 6.0 |
| Cetane number | 48 to 65 |
| Higher heating value, Btu/gal | 127042 |
| Lower heating value, Btu/gal | 118170 |
| Density, $kg/m^3$ at 15.5°C | 838.785 |
| Carbon, wt% | 77 |
| Hydrogen, wt% | 12 |
| Oxygen, by dif. wt% | 11 |
| Boiling point, °C | 315-350 |
| Flash point, °C | 100-170 |
| Sulfur, wt% | 0.0 to 0.0024 |

Biodiesel properties can change from one feedstock to the next. Biodiesel has lower carbon and hydrogen in comparison with diesel fuel, contains 11% of oxygen and about 10% lower energy content. Due to biodiesel's higher fuel density, its volumetric energy content is only about 5–6% lower than petroleum diesel [4].

The other main property of biodiesel fuel is its lubricating properties. Giving better lubricity and a more complete combustion, increases the engine energy output, thus partially balancing for the higher energy density of petrodiesel [4]. Adding biodiesel to fuel also helps in reducing fuel system wear, keep moving parts, especially fuel pumps, from wearing prematurely. It also provides horsepower, torque, and mileage similar to conventional diesel. Even in very low concentrations, biodiesel improves fuel lubricity and raises the cetane number of the fuel [3].

## 2.2 Advantages and disadvantages of biodiesel

Biodiesel has many major advantages, and some minor disadvantages:

Advantages of biodiesel are:

- ✓ Biodiesel is renewable. As biodiesel is produced from renewable sources, biodiesel fuel is a renewable energy source;
- ✓ In comparison with diesel fuel, biodiesel is safer and less toxic [5];
- ✓ Degrades more rapidly than diesel fuel, minimizing the environmental consequences of biofuel spills;
- ✓ Has lower emission of contaminants. When biodiesel is burnt, it's produced less carbon monoxide, unburned hydrocarbons and sulfur dioxide [6];
- ✓ Lower health risk. Although burning biodiesel produces carbon dioxide, but it doesn't contribute to global warming. The reason is the amount of carbon dioxide which plants take during growing is the same as the amount of carbon dioxide which is released during burning of biodiesel [6];
- ✓ Another of the advantages of biodiesel fuel is that it can also be blended with other energy resources and oils;
- ✓ B100 can reduce carbon dioxide emissions (which can raise the temperature and causes global warming) by 78% and lower the carcinogenic properties of diesel fuel by 94% [7];

- ✓ Biodiesel can be used in existing oil heating systems and diesel engines without making any changes;
- ✓ Another advantage of biodiesel in comparison with other alternative fuels is the possibility of distribution of biodiesel through existing diesel fuel pumps;
- ✓ The lubricating property of the biodiesel may lengthen the lifetime of engines [4];
- ✓ Higher flash point ($100^{o}$C minimum), which makes biodiesel less combustible. It is therefore safe to handle, store and transport [5,6].

Disadvantages of biodiesel:

There are certain disadvantages of using biodiesel as a replacement for diesel fuel that must be taken into consideration:

- ✓ Slightly higher fuel consumption due to the lower calorific value of biodiesel;
- ✓ Has slightly higher nitrous oxides (NOx) emissions than diesel fuel. In case of dissolving of NOx in atmosphere, it can cause acid rain [6];
- ✓ Higher freezing point than diesel fuel. Biodiesel gels in cold weather and it's may be difficult to use in cold climates (B100 is not suitable for use in cold weather);
- ✓ High cost, biodiesel fuel is currently more expensive than petroleum diesel fuel;
- ✓ It requires energy to produce biodiesel fuel from soy crops, plus there is the energy of sowing, fertilizing and harvesting;
- ✓ Biodiesel cleans the dirtiness from the engine. Although it is an advantage for biodiesel, but this dirt can then get collected in the fuel filter, thus clogging it. So, it damages filters and filters have to be changed after the first several hours of biodiesel use [4];
- ✓ Since biodiesel is produced from animal and vegetable fat, these reduce the amount of food and therefore increase the price of food, therefore it can cause to food crisis in many countries [6].

## 2.3 Benefits of biodiesel use

### Biodiesel reduces life-cycle greenhouse gas emissions

When biodiesel displaces petroleum, it helps to reduce: greenhouse gas (GHG) emissions, harmful particles which cause cancer and asthma, smog, ozone, carbon dioxide emissions and acid rain forming sulfur dioxide and some of the ills associated with burning petroleum diesel. It increases air quality. When plants such as soybeans 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 soybeans, it is converted into biodiesel. When the biodiesel is burned, $CO_2$ and other emissions are released and return to the atmosphere. Unlike diesel fuel this cycle does not add to the net $CO_2$ concentration in the air because as it was signed before (advantages of biodiesel) this soybean crop will reuse the $CO_2$ as it grows [3].

As biodiesel contains 11% of oxygen by weight it can reduce tailpipe particulate matter (PM), hydrocarbon (HC), and carbon monoxide (CO) emissions from most modern four-stroke internal combustion or diesel engines.

The use of B100 can eliminate as much as 90% of toxicities which are released during the diesel fuel combustion of particulate matter and hydrocarbons. The use of B20 reduces air toxics by 20% to 40% [3].

### Energy balance

Energy life cycle analysis is an energy balance that considers the amount of energy which is needed to produce the fuel and provides a way to compare the relative benefits among alternative fuel sources [8]. According to the biodiesel lifecycle studies by 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 [9]. This can be explained by biodiesel's closed carbon cycle [9]. Overall, from the energy balance (Table 2) it can be seen that for every unit of fossil energy needed to make biodiesel, 4.5 units of energy are gained [10]. It means that compared to regular fossil fuels, biodiesel has positive energy balance [9]. In other words, regular fossil fuels take more energy to produce than they provide in return [10]

Table 2 .Summary of Energy Balance / Energy Life cycle [10]

| Fuel | Energy Yield | Net Energy (Loss) or Gain |
|---|---|---|
| Gasoline | 0.805 | 19.5% |
| Diesel | 0.843 | 15.7% |
| Ethanol | 1.34 | 34% |
| Biodiesel | 4.5 | 350% |

Life cycle yield in liquid fuel. BTU's for each BTU of energy consumed [10].

**Biodiesel improves engine operation**

As diesel engines performance depend on the lubricity of the fuel it helps to keep moving parts, especially fuel pumps, from wearing prematurely. It also provides horsepower, torque, and mileage similar to conventional diesel. Even in very low concentrations, biodiesel improves fuel lubricity and raises the cetane number of the fuel. Biodiesel is better for car's engine than conventional diesel [3]. Just 1% of biodiesel added to petrodiesel is enough to increase lubricity to 65%, reduce mechanical problems and enhance the life and efficiency of engine [10] .
As biodiesel contains almost no sulfur or aromatics, so use of biodiesel in a diesel engine results in reduction of unburned hydrocarbons, carbon monoxide and particulate matter (PM) [7].

**Biodiesel is easy to use**

Finally, one of the biggest benefits to using biodiesel is that it is easy. No new equipment and no equipment modifications are necessary for using blends of B20 or lower. Unlike other alternative fuels, biodiesel can be used in most common diesel vehicle unmodified. B20 can be stored in diesel fuel tanks and pumped with diesel equipment. B20 does present a few unique handling and use precautions, but most users can expect a trouble-free B20 experience [3].

As was referred above replacing petroleum with biodiesel can solve many ecological problems. Like any fuel, biodiesel releases carbon dioxide while burning. But since biodiesel is produced from vegetable and animal fats, it cause less air pollution and does not contribute to global warming.

Using biodiesel reduces GHG pollutant emissions, unburned hydrocarbons, carbon dioxide, sulfur dioxide and many harmful particles, which can cause to illness.

Thereby we can diminish diseases, which contribute to thousands of untimely deaths each year. Users in environmentally sensitive areas such as wetlands, marine environments, and national parks have taken advantage of this property by replacing toxic petroleum diesel with biodiesel [3].

As we know, the transportation of raw materials may consume some additional fuel and take much time. Instead of importing resources from other countries, we can produce biodiesel using our own living resources. Thereby, we will save money, time, decrease energy expenses and as well it will develop economy of the country and can reduce country's dependence on fossil fuel [11].

**Compatibility**

Because of high flash point, biodiesel is less combustible and much safer than other fuels. Hence, it can be transported without any warning signs. Accordingly, producers can transport, pump, and store biodiesel using equipment already in place. Biodiesel can be blended and used in many concentrations. For example, B20 means that only 20% of biodiesel fuel is blended. The greater the percentage of biodiesel fuel in its blend, the more ecology-friendly is the fuel. Biodiesel mixes well with petrodiesel. It allows to fuel distributors to sell blends ranging from 5 to 100 percent biodiesel for use in diesel vehicles [12].

Biodiesel also has advantages in diesel engines. It increases cetane number and lubricity of fuels. Because of its higher flash point, it is a much safer fuel than any energy fuel in the market [11].

It is important to note that biofuel production and consumption, in and of itself, will not reduce GHG or conventional pollutant emissions, lessen petroleum imports, or alleviate pressure on exhaustible resources. Biofuel production and use must coincide with reductions in the production and use of fossil fuels for these benefits to accrue. These benefits would be mitigated if biofuel emissions and resource demands augment, rather than displace, those of fossil fuels [13].

## 2.4 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 [14].

As the consequence of the Fuel Quality and Renewable Directives in mid-December the EU is rising its B5 standard to B7. The new standard can be applied within next two years by the member countries of EU while The Fuel Quality Directive will phase the aims in climate change reduction over the next ten years. The member states get a way to adjust their standards according to EU's Fuel Quality Directive until June publication of the new standard by The European Committee for Standardization (CEN). The renewable energy increase policy includes obligatory 10% goal for fuels such as hydrogen, biofuels and electricity. This new requirement replaced 5.75% goal of 2010 which was determined in 2003 and adjusted by some member countries through different local policies. As the result of long discussion about degreasing targets, the 2003 goal about 10% for biofuels in 2020 was kept as an obligatory aim [15].

Figure 1 illustrates the investment of different counties and regions to biodiesel production in 2009-2010 [16].

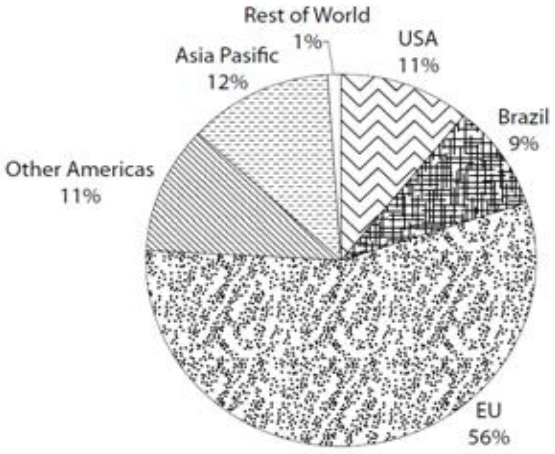



Figure 1. Biodiesel production in different countries [16]

**Biodiesel Consumption**

As it can be seen from Figure 2, there was observed a very slight increase of liquid biofuels in 1990. There were sharply increases-mainly after 2002. The percentage of producing continued to rise gradually over the ten year period from 2000-2010 (about 32%) [17]. According to the European Biodiesel Board statistics, overall EU production decreased significantly in 2011, reaching 8.6 million tones [18]. However, production decreased in 2011 by 10% compared with 2010 [17]. Yet, as biodiesel represents the main renewable alternative to fossil transport, biodiesel consumption is expected to rise [18]. Since then it has been increasing at around 10% per year [17].

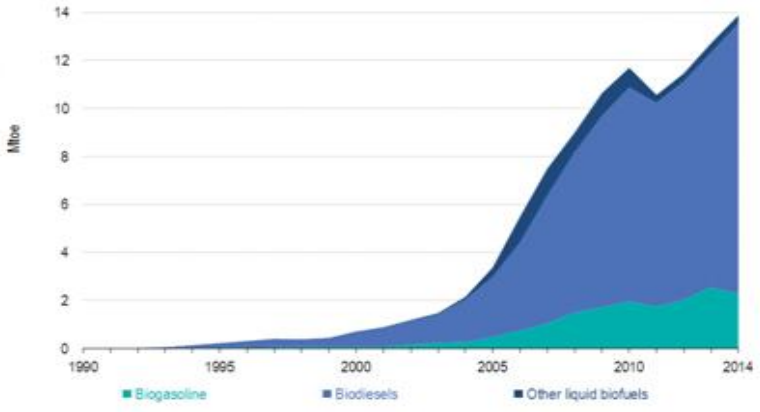



Figure 2. Production of biodiesel in Europe [17]

## 2.5 Raw materials for biodiesel production

Biodiesel has been mainly (more than 95%) produced from edible vegetable oils, animal fats and short chain alcohols all over the world, which are easily available on large scale from the agricultural industry [2]. The oils most used for worldwide biodiesel production are rapeseed (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils, and also animal fats. The most frequently used alcohol for biodiesel production is methanol [5].

But from economic and social side of view using edible oils, because of increasing the food prices can lead to food crisis. Moreover, these oils could be more expensive to use as fuel. Thus edible oils can be replaced by lower-cost secure feedstocks for biodiesel production such as non-edible plant oils [19].

As non-edible oil feedstock, can be use castor oil and jatropha, tung, cotton, jojoba and microalgae oil, which proved to be highly promising reliable sources, having high oil content.

Algae oil, due to its availability and low cost is considered as an economical choice for biodiesel production [20].

Animal fats are also an interesting option, especially in countries with plenty of livestock resources, although it is necessary to carry out preliminary treatment since they are solid; furthermore, highly acidic grease from cattle, pork, poultry, and fish can be used.

Microalgae appear to be a very important alternative for future biodiesel production due to their very high oil yield; however, it must be taken into account that only some species are useful for biofuel production. Although the properties of oils and fats used as raw materials may differ, the properties of biodiesel must be the same, complying with the requirements set by international standards [5].

## 2.6 Production of biodiesel

The American Standard Test Methods (ASTM) defined biodiesel as "a fuel comprised of monoalkyl esters of long-chain fatty acids produced from vegetable oils or animal fats, designated B100". Biodiesel production can be obtained by different catalytic processes such as alkali-catalyzed, acid-catalyzed and enzyme-catalyzed reactions [21].

Alkali catalyzed processes require high amounts of alcohol and high pressure (170-180 kPa), which force the increase of the reactor size, and also require comprehensive conditioning and the purification of unreacted alcohol and catalyst from the products. All these disadvantages will affect to biodiesel price [22]. Enzyme catalyzed processes are environmentally friendly and very selective, but due to high cost and ineligible activities, they are not applicable for the industry scale [21]. The most common reactions for biodiesel production are transesterification of triglycerides or esterification of free fatty acids (FFAs) in presence of alcohol to produce fatty acid alkyl esters (FAAEs) [23].

There are several methods of biodiesel production which are illustrated in Table 3.

Table 3. Methods of biodiesel production [24]

| **Process** | **Feedstock** | **Product** |
|---|---|---|
| Esterification | Free fatty acids | Fatty acidy methyl ester (FAME)+ Glycerol |
| Hydrotreating | Vegetable oils and animal fat | Hydrotreated vegetable oil (HVO) + Paraffin |
| Gasification<br>+<br>Fischer Tropsch | Wood, energy crops,agriculture residues, waste, etc. | Biomass to liquid fuel (BTL) |
| Transesterification | Triglycerides | Fatty acid alkyl ester + glycerin |

## 2.6.1 Transesterification

The one of the accepted processes of biodiesel production is transesterification, process by which the triglycerides are reacted with alcohols, in the presence of a catalyst, to produce fatty acid alkyl esters (Figure 3). A byproduct of transesterification is glycerin, also known as glycerol. The most common alcohol, which is used in biodiesel production is methanol, another name for biodiesel is fatty acid methyl esters (FAME) [4].

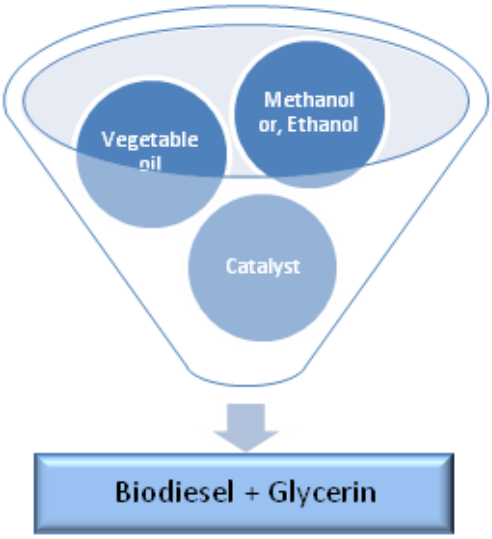



Figure 3. Catalytic transesterification [14].

The process itself, in principle, is quite simple. It is necessary to reduce the viscosity of vegetable oils, which can be achieved in various ways. Any vegetable oil - a mixture of triglycerides, i.e. esters, connected to a glycerol molecule with trihydric alcohol. The glycerol gives a viscosity and density of the oil. The challenge in the preparation of biodiesel is to remove glycerin, replacing it on the alcohol. As a result of using the methanol as alcohol, a methyl esters are formed [25]. The transesterification process occurs according to the chemical equation 1, as represented in Figure 4.

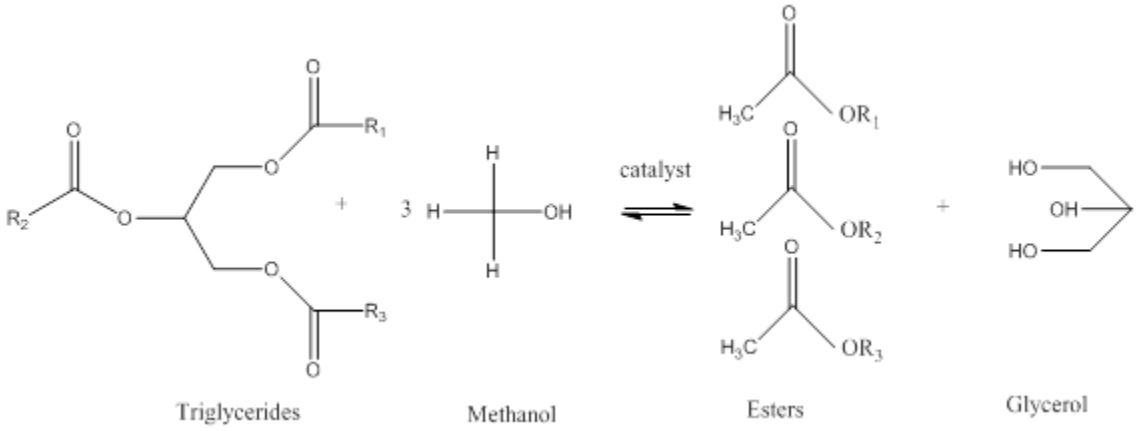



Figure 4. Biodiesel synthesis by transesterification process from vegetable oils with methanol [26].

Among the different type of catalysts used (i.e. alkali, acid and enzyme based), alkali based catalysts are most widely used in industrial processes because it is more effective and less corrosive to the industrial equipment [14].

The calculated amount of alkali (usually NaOH) needed is calculated by titration of the oil, and slowly dissolved with stirring in an excess of alcohol (for a more complete reaction). The mixture is then added to the pre-heated warm oil (normally to about 50°C), also with stirring for several hours (4-8h), to undergo the transesterification reaction. The reaction mixture is normally maintained above the boiling point of the alcohol, but in some systems for safety reasons it is recommended to maintain the temperature range from room temperature to 55°C. Usually the reaction time is from 1 to 10 hours, and under normal conditions, the reaction rate is doubled by raising the reaction temperature 10°C. To prevent evaporation of the alcohol the reaction should be carried out in a closed container, but it is important to avoid a sealed system (because of risk of explosion) [25]. In Figure 5 was represented the basic technology of biodiesel production.

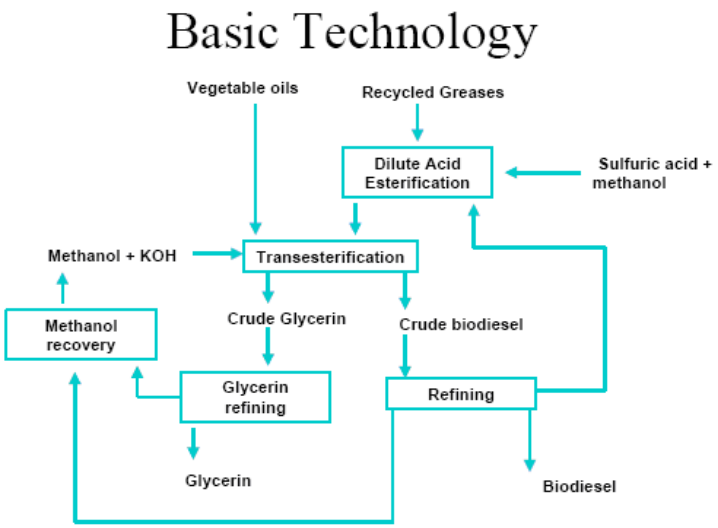



Figure 5. Technology of biodiesel process [25]

However, there are many disadvantages including low reaction rate, low activity, low stability, high temperature, long reaction time, moisture sensitivity of the catalyst, high cost, saponification (in result of reaction of water with $Na^+$ ions) and, difficulties in downstream recovery and purification of the product [37].

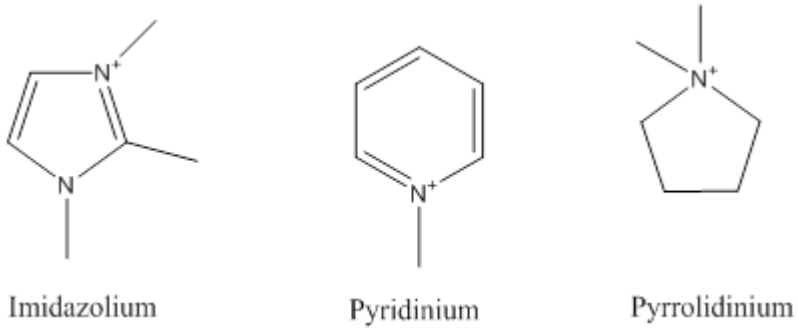
Nowadays, these catalysts can be replaced by ionic liquids, which can be used as solvents or catalysts for esterification and transesterification reactions [21].

## 3. Ionic liquids

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. Early in the 20th century (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. Their research involved the replacement of the LiCl-KCl molten salt electrolyte used in thermal batteries, but it was resulted with serious problems with air-sensitivity and electrochemically reduction. Later, in 1990, the professor from US Air Force Academy, Dr. Mike Zaworodko discovered the solution which gave a new dimension for the using of ionic liquids in electrochemistry. Since then, IL due to its unique properties and possibility in use had an important role in scientific researches and also in industries [27].

Ionic liquids (IL) are defined as liquid state molten salts at low temperatures (below than $100^{o}$C). They are composed of organic cations and either organic or inorganic anions, and were used as solvents/catalyst for reaction [28]. It is important to note that while these compounds may actually be solid at room temperature, they are typically referred to as liquids because they have a melting point below $100^{o}$C [29].

***Cations***

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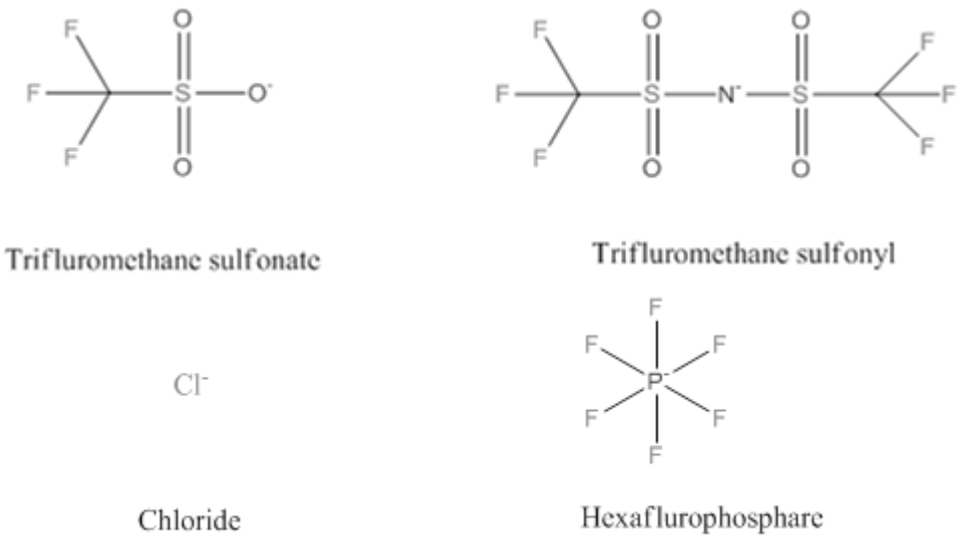


Figure 6. Composition of ionic liquids [27]

## 3.1 Types of ionic liquids

According to the cations, ionic liquids are divided into four groups: quaternary ammonium ILs, N-alkylpyridinium ILs, N-alkyl-isoquinolinium ILs, and 1-alkyl-3-methylimidazolium ILs [30]. Quaternary ammonium salts ("quats") because of its surface-active properties, possess anti-microbial activity are an economically advantageous class of industrial compounds [31].

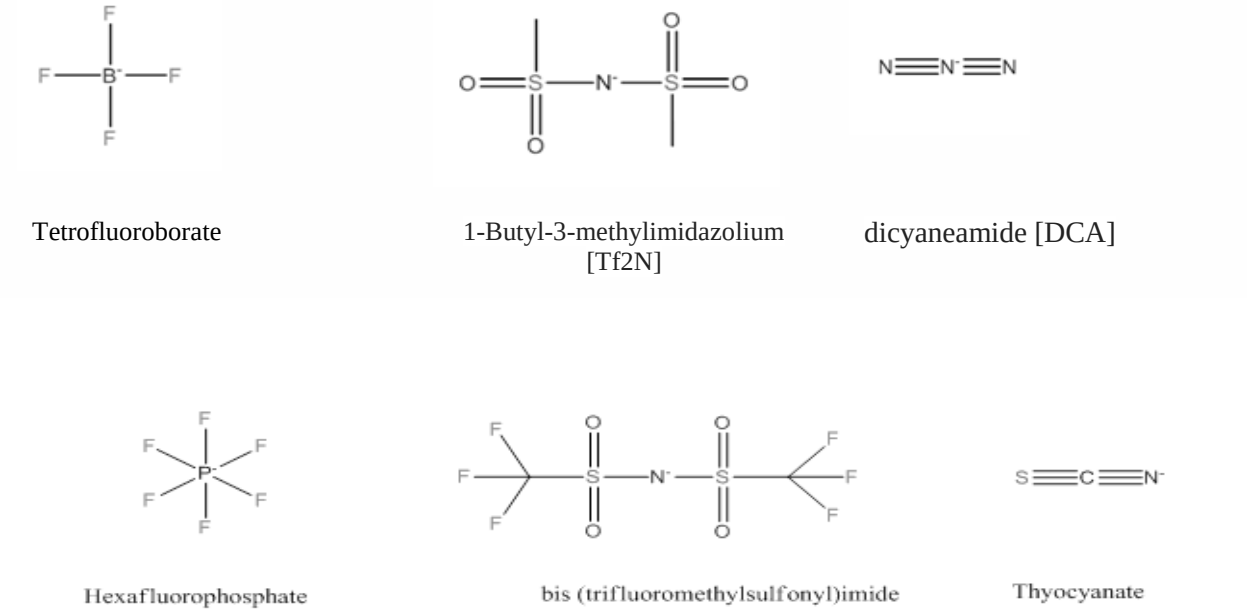


Figure 7. Selected anions of phosphonium- and ammonium-based ILs [31]

Zhang *et al.* (2003) [32] researched 1-alkyl-3-methylimidazolium and N-butylpyridinium salts (Figure 8) as new mobile phase additives for separation of catechol amines, epinephrine, norepinephrine and dopamine by reversed-phase high-performance liquid chromatography analysis. They studied the effect of different pH values of the mobile phase, concentration of ionic liquids, and different alkyl substituents on the cations or different counter-ion of ionic liquids as it influence the separation of compounds. The separation mechanism involves molecular interactions between ionic liquids and catechol amines [27].

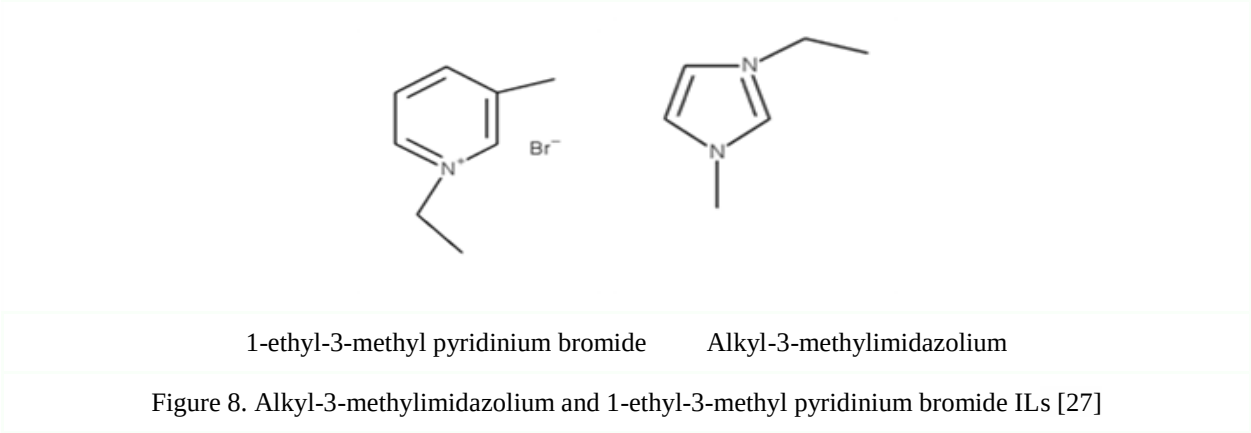


Figure 8. Alkyl-3-methylimidazolium and 1-ethyl-3-methyl pyridinium bromide ILs [27]

A series of hydrophobic n-alkyl-N-isoquinolinium ionic liquids (ILs) with a linear alkyl-chain substituent containing from 4 to 18 carbon atoms in combination with hexafluorophosphate, bis (trifluoromethylsulfonyl) amide, and bis- (perfluoroethylsulfonyl) amide have been synthesized and characterized (water content, density). The crystal structures of [C2isoq][PF6] (prepared and isolated only for the comparative X-ray diffraction study), [C4isoq]- [PF6], and [C10isoq] [PF6] illustrate the underlying interactions in the higher melting salts. The isoquinolinium-based ILs are interesting due to their highly aromatic nature and physical and solvent properties [30].

Certain ILs that are regarded as ‘‘green’’ solvents have received worldwide attention in various fields including catalysis, electrochemistry, separation, and inorganic nanomaterials, among others. In a pioneering study by Rogers *et al.* (2002) [33], several ILs, in particular, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), were found to be capable of dissolving up to 25% cellulose (by weight) [34].

## 3.2 Ionic liquid properties

Because of the wide range of properties, ionic liquids was accepted as a new green chemical that is capable of revolutionizing chemical processes [35]. The ionic liquids possessed greener properties such as very low relative volatility i.e., close to zero, wide liquids temperature and significantly less toxic compared to the organic solvent.

They can also be made miscible or immiscible with organic solvents and water.

Both could be achieved by simply varying their anion–cation combinations. Because of these, ILs possesses numerous advantages over the conventional organic solvents, besides more environmentally compatible [36]. Moreover, they can be colorless, non-flammable, have high catalytic activity, low viscosity, potential recyclability, and are easily manipulated and environmentally friendly.

The most interesting characteristic of ionic liquids is the possibility of designing a molecule aiming at a specific application or in order to obtain a certain set of properties such as melting point, viscosity, density, water solubility and selectivity [35].

Besides their use as solvents, 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 Brønsted acidity or basicity. Brønsted acidic ILs, were highly efficient catalyst for biodiesel synthesis from vegetable oils. Sulfuric acid groups in these ILs are the active sites for transesterification [28]. In Table 4, there are represented different yields with varying ionic liquids.

If we compare yields of KOH and ionic liquids, KOH showed similar activity, but it is very difficult to recycle and produce a large amount of wastewater during the production process. Also ionic liquids are much less sensitive to water and free fatty acid [37].

In some cases using ionic liquids without metal ions does not give desirable yields. For example, 1butyl-3methyl imidazolium methanesulfonate [BMIM][$CH_3SO_3$] (Brønsted acidic acid) had the highest catalytic activity with 93% esterification rate for oleic acid at 140$^oC$, but only 12% biodiesel yield at 120$^oC$. But if we add $FeCl_3$ to the [BMIM][$CH_3SO_3$], the yield of biodiesel will increase up to 99.7% at 120$^oC$.

It occurs, because of providing of metal ions in ILs with Lewis acidic sites, and these sites could be provided by trivalent metallic ions than those of bivalent ones. The IL [BMIM][$CH_3SO_3$] and $FeCl_3$ can be easily separated and reused [28].

Table 4. Types of some ionic liquids as solvents for biodiesel production and its yields.

| | | | | |
|---|---|---|---|---|
| **Methanol/soybean oil** Ratio 8:1 [37] | [Hnmm]OH 4% | 70$^{o}$C | 1.5 h | 97% |
| **Methanol/Jatropha oi**l Ratio 6:1 [28] | [BMIM][$CH_3SO_3$]-$FeCl_3$ | 120$^{o}$C | 5 h | 99.7% |
| **Methanol /Crude palm oil** Ratio 12:1 [22] | (BMIMHSO4) 4.5wt % | 160$^{o}$C | 120 min | 98.4% |
| **Triolein** [38] | [$C_8$mim][$NTf_2$] | 60$^{o}$C | 6h | 96% |
| **Myglyol oil** [38] | Chlorine acetate | 40$^{o}$C | 3h (chlorine acetate/ glycerol 1:1:5) | 97% |
| **Soybean oil** [38] | [$C_4$mim][$NTf_2$ ] | Room Temperature | | 96% |
| **Cooking oil** [38] | 1ethyl,3methyl Imidazolium trifluromethane sulfonate | 40$^{o}$C | 24h | 99% |
| **Soybean oil** [38] | [$C_2$mim][TfO] | 50$^{o}$C | 12h | 80% |
| **Triolein** [38] | [$C_{16}$mim][$NTf_2$] | 60$^{o}$C | 24h | 99% |

## 3.3 Imidazolium based ionic liquids

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. This type of ionic liquids is progressively used as green solvents to replace the volatile and relatively toxic organic solvents, in homogeneous and heterogeneous catalysis, materials science, nanomaterials, lithium ion batteries, and separation technology [39-41].

Table 5. Melting point of some popular imidazolium cation based ILs [42]

| Imidazolium ILs | Melting point T (ºC) | Viscosity η (cP) |
|---|---|---|
| BmimBr | 79 | solid |
| HmimBr | -54.9 | 3986 |
| Pmiml | -56 | 35 |
| Bmiml | -72 | 1110 |
| Hmiml | -72 | 771 |
| $BmimBF_4$ | -81 | 219 |
| $BmimPF_6$ | 4 | 450 |
| $HmimPF_6$ | -61 | 585 |
| $EmimNTf_2$ | 4 | 28 |
| $BmimNTf_2$ | -25 | 69 |

## 3.4 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, for highly concentrated oils the acid catalyst (most common sulfuric and sulfonic acids) are especially used. But these reactions has some disadvantages like long reaction time (from 48 to 96 hours), use of large amounts of alcohol to achieve biodiesel in satisfactory yields and the risk of the equipment corrosion due to the high acidity of the catalysts [35].

The possibility of recovery and reuse of ionic liquids minimizes the waste in catalytic reactions, among the options which are currently studied; the use of ionic liquids in catalytic systems seems to be environmentally secure.

Through the ionic liquids insoluble in the organic phase and remains in the aqueous phase along with alcohol, in the transesterification reaction in the end the biphasic system is form and the used catalyst and glycerol produced during the reaction.

The organic phase consists almost completely of biodiesel. The solubility of glycerol in an ionic liquid/ methanol mixture is an advantage of the system. Therefore, the removing of the glycerin from the reaction shifts the reaction equilibrium to the product formation, and this increases the reaction yield [35].

Ionic liquids have been used in a large number of chemical reaction types. The main advantage of using ionic liquids in reactions is their non-volatility except at high pressures and low temperatures, and also their properties can be used to suit a particular need ("designer" solvents).

As a designer solvent, it can change the structure of ionic liquids, such that it phase separates from the product of a reaction, making product isolation easier. Another method is to make either the cation or anion or both of the ionic liquids acidic or basic (either Lewis or Brønsted). This method gives an opportunity to the ionic liquid to catalyze esterification, transesterification, and specifically biodiesel forming reactions. Through this design ability, the ionic liquids in the end of the reaction can be fully recovered without any ionic liquid waste. But the disadvantage of this ionic liquids is that, they are more expensive that simple catalysts and conventional solvents [43].

## 3.5 Methods for recovery of ionic liquids

There are a restricted number of industrial processes utilizing ILs due to their high cost. To overcome the cost problem of ILs an efficient recycling of ILs is important for their industrial use, particularly for pilot-plant applications [44].

After recovery IL the physical properties of recovered IL remained unchanged and the recovered ILs were reused at least four times without loss of their purity [50].

Moreover, during the industrial use, they might be blended with other products, which require an efficient separation too. In addition, recovery of ILs is also important to resolve the environmental troubles of the removal, like biodegradation and toxicity [44].

The ILs that contains both hydrophilic and hydrophobic domains (surfactant-like ILs, e.g. ILs possessing long aliphatic substituents) generates micelle in water. The micellization of ILs depends on the size of these domains (larger the hydrophobic domain, greater the tendency to aggregate). These combined ILs can be separated by filtration or centrifugation. It's easier to recover hydrophobic ionic liquids than hydrophilic. For example, it needs too much energy to distillate diluted aqueous solutions and hence it makes the recovery process impracticable [44].

Kanel (2003) mentioned some of the methods that have been studied to recover and reuse ILs like heating or evaporation of volatiles under vacuum, extractions with VOC (volatile organic compounds) solvents (obviate some of the advantages of using ILs), supercritical CO2 extraction, and distillation/stripping of the solute from the ILs (for thermally stable ILs) [45]. It is possible to recover ILs by distillation from compounds of low boiling points as their vapor pressure has any considerable effect in the process. Furthermore, distillation can be used for recovering thermo-stable compounds which boiling points differ from IL.

According to the BASF company studies recycling of IL might be easy if protonated cations are used. In this case the ILs can be switched off by deprotonation. Imidazolium cations can be deprotonated by bases to form neutral carbene molecules. The resulting carbenes (amine or imidazole) are found surprisingly stable and can be distilled for recycling or purification purposes [45].

# 4. Experimental

### 4.1 Chemicals and solvents

- Ionic liquid [BMIM]$HSO_4$ (1 butyl 3 methylimidazolium hydrogen sulfate), used as a catalyst with purity ≥94.5%, from Sigma Aldrich (Switzerland);
- Oleic acid with purity of 90% Ph. Eur from Sigma Aldrich (Belgium);
- Methanol Panreac for HPLC (99.9%);
- pH indicator phenolphthalein solvent diethyl ether from Panreac Quimica SA (Spain);
- Absolute ethanol from Fisher Scientific UK;
- Hydrochloric acid (Fisher Chemicals, UK);
- 37 Component FAME Mix from Supelco.

### 4.2 Production of biodiesel

The esterification was carried out in a 100 mL glass reactor with continuous stirring, connected to reflux condenser and thermometer (Figure 9). The calculated amounts of oleic acid and ionic liquid were firstly mixed in the reactor which was then immersed into a bath (water bath or paraffin, depending on the temperature) and heated to the desired temperature, then methanol was added to the reactor. The solution was continuously stirred at 300 rpm using a magnetic stir-bar at a specified temperature, time, oleic acid/methanol molar ratio and ionic liquid percentage.

Figure 9. Experimental apparatus for the esterification process

After reaction reached to the desired time, the reaction was stopped; the reactor was removed from the bath, and cooled to room temperature. After reaching room temperature, mixture was separated by centrifugation (Figure 10) during 20 minutes at 3000 rpm.


Figure 10. Sigma centrifuge equipment (Model 2-4).

The obtained conversion of the reaction was measured by titration with a standard alcoholic solution of potassium hydroxide with concentration 0.1M

Additionally, all samples were analyzed by gas chromatography in order to measure qualitatively and quantitatively its FAMEs (Fatty Acid Methyl Esters) content (% Area and % m/m). For quantitative determination an internal standard compound (heptadecanoic acid methyl ester) was used with concentration of 10mg/mL.

### 4.2.1 Acidity measurement procedure

1) KOH solution preparation (using methanol as solvent): 5.6g of KOH diluted in 1L of methanol

2) Titration of KOH: using a HCl previously titrated (already prepared) standard solution. Measure 1/2 volume ratio of HCl/distilled water (10 mL of HCl and 20 mL of distilled water) and 5 drops of phenolphthalein and titrate until reaching light pink color.

The concentration of KOH solution was calculated using the following formula:

$$C_{KOH} = \frac{V_{HCl} * C_{HCl}}{V_{KOH}} \qquad (1)$$

where,

$V_{HCl}$ is the volume of HCl used for titration (mL)

$C_{HCl}$ is the concentration of HCl (mol/L)

$V_{KOH}$ is the volume of KOH used for titration (mL)

3) Acid value determination of biodiesel

The standard method to measure the acid value of biodiesel is a volumetric titration (acidity is expressed in mg KOH/g oil) using standard solution of KOH with concentration of 0.1 mol/L (Method EN 14104:2003). A solution of 1:1 diethyl ether/ethanol was used as solvent for volumetric titration. Phenolphthalein was used as the indicator.

3.1) First, 40 mL of solvent (Diethyl ester/Ethanol 1/1) was neutralized adding 5 drops of phenolphthalein and stirring the mixture then add some drops of KOH standard solution from the burette to neutralize solution until the color changes to light pink.

3.2) Then 1 mL of obtained biodiesel product was weighed using a precision balance, and titrated with the same solvent, until reaching pink color.

The acid value of biodiesel was calculated with the formula

$$Acid\ value, AV\ \left(\frac{mgKOH}{gbiodiesel}\right) = \frac{V * C_{KOH} * M_{w(KOH)}}{m_{biodiesel}} \qquad (2)$$

Where

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

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

$M_w$ - molecular weight of KOH =56.1 (g/mol)

$m_{biodiesel}$ -weight of biodiesel (g)

### 4.2.2 Determination of the production yield

After obtaining the acid value, the biodiesel conversion was calculated using the following equation:

$$\text{Production Yield, Y}(\%) = \frac{A_i - A_f}{A_i}\ x\ 100 \qquad (3)$$

where

$A_i$ – acidity of oleic acid (initial), $(mg_{KOH}/g_{oleic\ acid})$

$A_f$ – acidity of sample (final ) after reaction $(mg_{KOH}/g_{biodiesel})$

### 4.2.3 Fatty Acid Methyl Ester (FAME) content

The FAME content in all samples was determined using Gas Chromatography (GC).

All analyses were carried out on a Varian 3800 GC equipment (Figure 11), equipped with a Supelcowax 10 column (30mx0.25mmx0.25µm) and with flame ionization detector (FID). The injector temperature was set to 250$^{o}$C. Injector mode in split 1:20, total running time 85min.

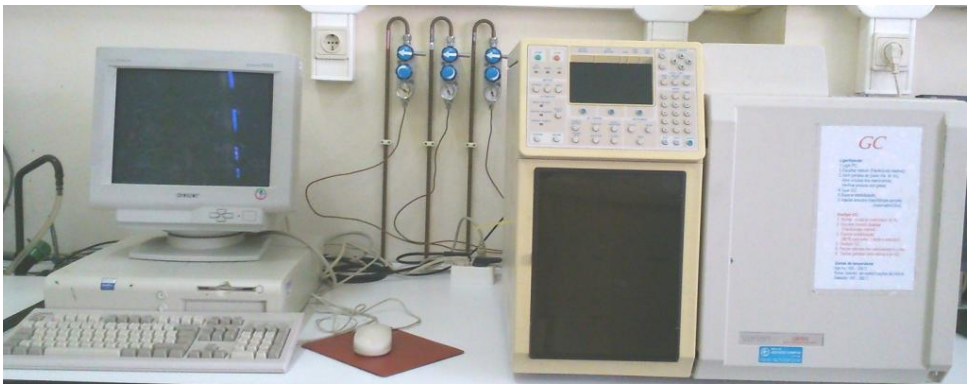


Figure 11. Varian 3800 GC equipment

The oven temperature program was previously optimized and set as: temperature held 50°C for 2 minutes then increased for 4°C/min until reaching 220°C (Figure 12).

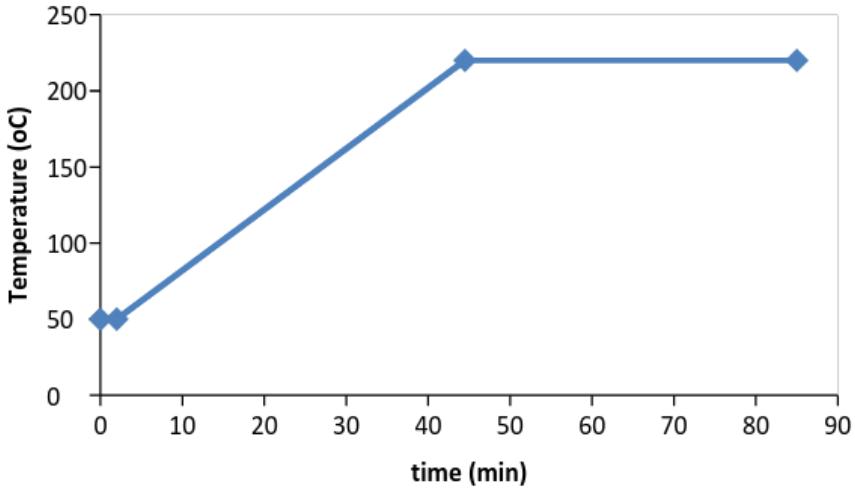


Figure 12. Oven temperature program used in the GC method.

**Sample preparation**

1) Measure 250mg of biodiesel to a 10 mL flask.
2) Prepare internal standard solvent: mix 500 mg of methyl heptadecanoate with 50 mL n-heptane. Add 5 mL of solvent to the flask with biodiesel.
3) Shake the solution and let it stand for 1 minute.
4) Dry the solution adding a micro-spatula of anhydrous sodium sulfate, and let it stay for 5 minutes before injection.

**GC analysis**

For injection of the sample, syringe needle should be inserted into the injector inlet. Press the syringe barrel against the injector switch and depress it completely, simultaneously pressing down the syringe plunger. Remove the syringe from the injector immediately. The RUN light comes on and stays on until the analysis ends [46].

The obtained chromatogram results were compared with the 37 FAME mix Supelco Sigma standard solution (Figure 13). To compare results for analyzing FAMEs was evaluated the Supelco 37 Component FAME Mix Omegawax capillary column, which is equivalent to Supelcowax column and has the same column packed material (Figure 14).

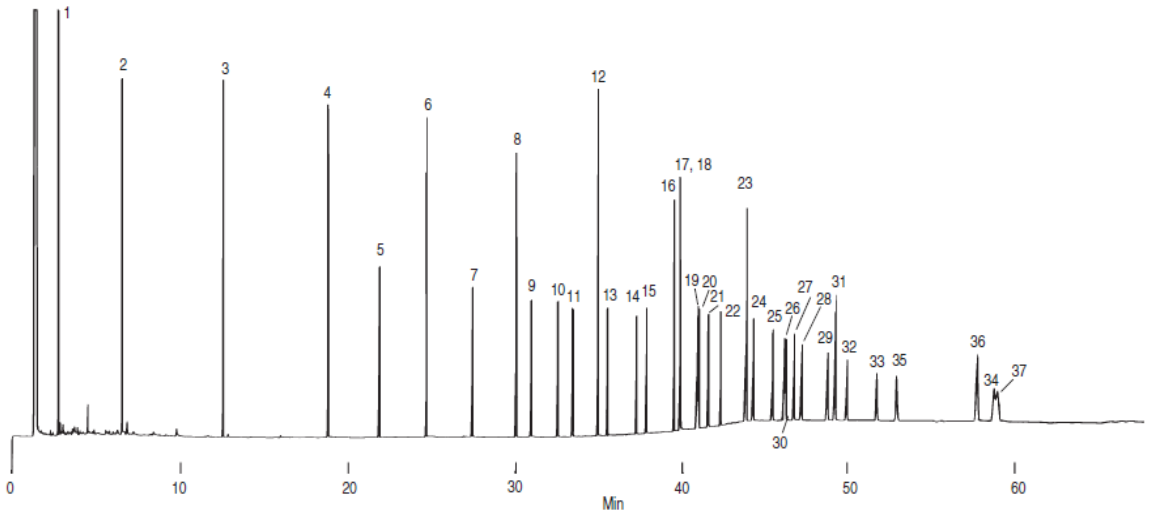


Figure 13. Supelco 37 Component FAME Mix using a Omegawax 250 Column [47]

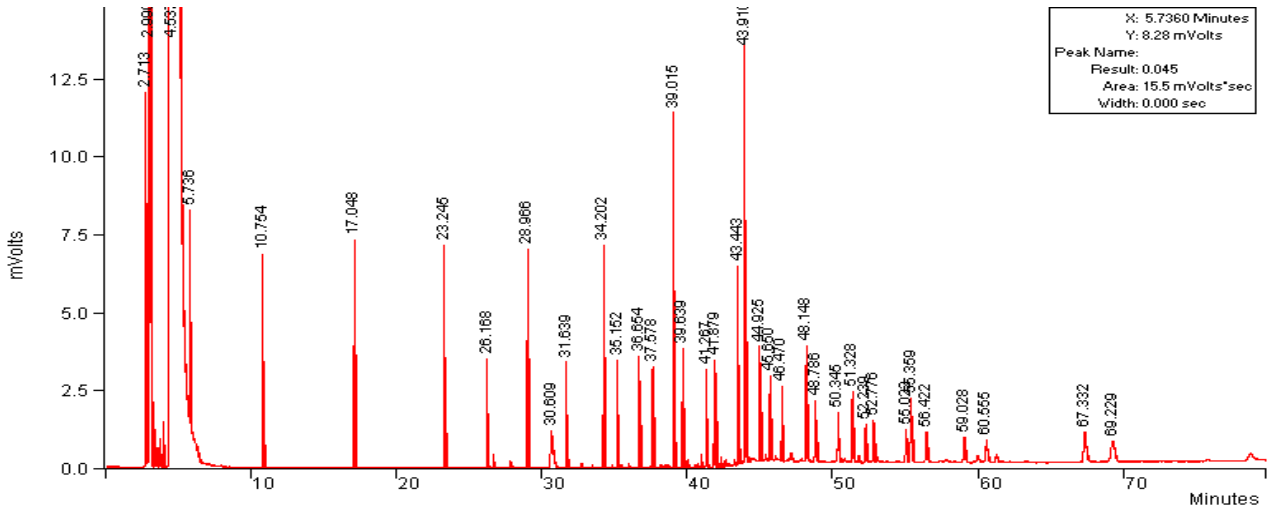


Figure 14. Supelco 37 Component FAME Mix using the Supelcowax 10 Column.

By comparing obtained results with Supelco 37 Component FAME mix the order for all 37 compounds can be identified (Table 6)

Table 6. Identification of FAME compounds present in the standard mixture solution using the Varian GC and operation conditions presented in section 4.2.3.

| Peak ID | Acid Methyl esters | Time (min) |
|---|---|---|
| 1 | C4:0 (Butryic) | 5.736 |
| 2 | C6:0 (Caproic) | 10.754 |
| 3 | C8:0 (Caprylic) | 17.048 |
| 4 | C10:0 (Capric) | 23.245 |
| 5 | C11:0 (Undecanoic) | 26.168 |
| 6 | C12:0 (Lauric) | 28.966 |
| 7 | C13:0 (Tridecanoic) | 31.639 |
| 8 | C14:0 (Myristic) | 34.202 |
| 9 | C14:1 (Myristoleic) | 35.152 |
| 10 | C15:0 (Pentadecanoic) | 36.654 |
| 11 | C15:1 (cis-10-Pentadecenoic) | 37.578 |
| 12 | C16:0 (Palmitic) | 39.015 |
| 13 | C16:1 (Palmitoleic) | 39.639 |
| 14 | C17:0 (Heptadecanoic) | 41.267 |
| 15 | C17:1 (cis-10-Heptadecenoic) | 41.878 |
| 16 | C18:0 (Stearic) | 43.443 |
| 17/18 | C18:1n9c (Oleic)/ C18:1n9t (Elaidic) | 43.910 |
| 19/20 | C18:2n6c (Linoleic)/ C18:2n6t (Linolelaidic) | 44.925 |
| 21 | C18:3n6 (γ-Linolenic) | 45.650 |
| 22 | C18:3n3 (α-Linolenic) | 46.470 |
| 23 | C20:0 (Arachidic) | 48.148 |
| 24 | C20:1n9 (cis-11-Eicosenoic) | 48.786 |
| 25 | C20:2 (cis-11,14-Eicosadienoic) | 50.345 |
| 26 | C20:3n6 (cis-8,11,14-Eicosatrienoic) | 51.358 |
| 30 | C21:0 (Henicosanoic) | *NI* |
| 27 | C20:3n3 (cis-11,14,17-Eicosatrienoic) | 52.239 |
| 28 | C20:4n6 (Arachidonic) | 52.776 |
| 29 | C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic) | 55.022 |
| 31 | C22:0 (Behenic) | 55.359 |
| 32 | C22:1n9 (Erucic) | 56.422 |
| 33 | C22:2 (cis-13,16-Docosadienoic) | 59.028 |
| 35 | C23:0 (Tricosanoic) | 60.555 |
| 36 | C24:0 (Lignoceric) | 67.332 |
| 34/37 | C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic) /C24:1n9 (Nervonic) | 69.229 |

### 4.2.4 Determination of ester content

In EN 14103:2003, the result for the fatty acid methyl ester content is expressed as a mass fraction in percentage using methyl heptadecanoate (C17:0) as the internal standard.

The FAME content was measured using two different methodologies: qualitatively method using the chromatographic areas (%), and qualitatively using the internal standard method (%m/m) as described in the EN 14103:2003 and using the following equation:

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

where,

ΣA - is the total peak of area from the methyl ester in $C_{14}$ to that in $C_{24:1}$

$A_{EI}$ - is the peak of area corresponding to methyl heptadecanoate

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

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

m - is the mass of the sample, mg

The methyl ester area and the total FAMEs area were calculated using the equations:

$$\%\, FAME_i = \frac{A_i}{\Sigma A_{FAMEs}} * 100\% \qquad (4)$$

$$\%FAME_{TOTAL} = \frac{\Sigma A_{FAMEs}}{A_T} * 100\% \qquad (5)$$

where,

$A_i$ - is area of component (%)

$\Sigma A_{FAMEs}$ - is the total area of FAMEs (%)

$A_T$ - is the total area of peaks (%)

### 4.3 Development of the experimental methodology

The influence of different reaction parameters on the biodiesel yield was studied in this work. Optimization parameters are classified into four main sections: 1) reaction time (h); 2) reaction temperature ($^oC$); 3) oleic acid /methanol molar ratio 4) ionic liquid amount (%wt).

In the experiments described below the biodiesel yield was measured using different reaction times (1-2-3-4-6 hours), reaction temperatures studied were 60-70-80-90-100-110$^oC$, with the Oleic Acid/Methanol molar ratio ranging from 1/1; 1/2; 1/5; 1/10, for different percentages (2.5; 5; 7.5; 10; 12.5 wt%) of [BMIM]$HSO_4$ ionic liquid.

# 5. Results and discussion

## 5.1 Optimization of biodiesel production

### 5.1.1 Reaction time

The reaction time is an important factor, which influence the biodiesel yield. The reaction time was studied within the range between 1h and 6h. Experimental results presented in Figure 15 show that the increase of the reaction time shifts the reaction equilibrium to the products, thus increasing biodiesel yield. According to this plot, it can be seen that the biodiesel yield gradually increases from 1h and thus keeps going up. However, as the difference among yields is not significant, optimization value can be considered as 4h, however, with the further increase in time the biodiesel yield may also increase.

All studied reaction parameters are presented in Appendix B, Table B1.1

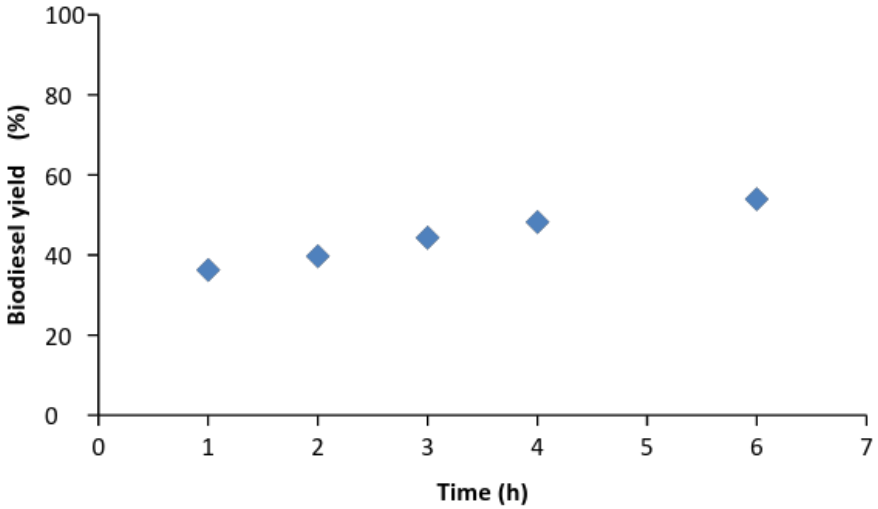


Figure 15**.** Effect of the reaction time on the biodiesel yield (Reaction parameters: 80$^{o}$C, 1/2 Oleic acid/methanol molar ratio, 10% IL).

### 5.1.2 Reaction temperature

The temperature is one of the most important factors that can influence the reaction yield of biodiesel production. In the following set of experiments the biodiesel was studied yield using a temperature range from 60$^{o}$C to 110$^{o}$C using a reaction time of 4h (see Appendix B, Table B1.2). Increase in reaction temperature speeds up the reaction rate, and therefore increases the product yield. Results obtained in these experiments show that increasing of temperature clearly influences the biodiesel yield (Figure 16). As it can be seen from experimental results the conversion gradually increased with the temperature rise, and after reaching 90$^{o}$C remained nearly at stable position. Further increasing of temperature (100 and 110$^{o}$C) did not lead to significant rising in biodiesel yield, indicating that the reaction is close to equilibrium. As a consequence, it can be consider 90$^{o}$C as an optimum temperature.

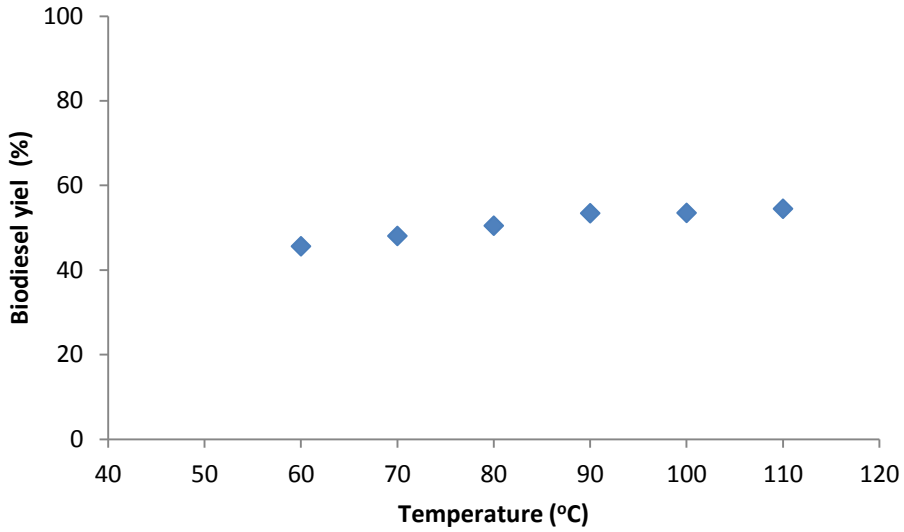


Figure 16. Effect of the reaction temperature on the biodiesel yield conversion. (Reaction parameters: 4h, 1/2 Oleic acid/methanol molar ratio, 10% IL)

### 5.1.3 Oleic Acid / Methanol molar ratio

Another important parameter, which has effect on the biodiesel yield is oleic acid/ methanol molar ratio.

In order to achieve the best conditions for biodiesel production, the experiments were carried out at a temperature of 90$^{o}$C, with a reaction time of 4h and using oleic acid/ methanol molar ratios of 1/1, 1/2, 1/5, 1/10, 1/15 (Appendix B, Table B1.3). The obtained experimental results are presented in Figure 17. As shown in Figure 19, biodiesel yield at reaction time 4h and at 90$^{o}$C significantly increased with increasing methanol concentration. At optimum conditions, higher molar ratios result in greater biodiesel conversions. The maximum point was achieved at 89.7% using oleic acid /methanol molar ratio 1/10. According to the experimental results, the optimal molar ratio of methanol to oleic acid was considered to be 1/10.

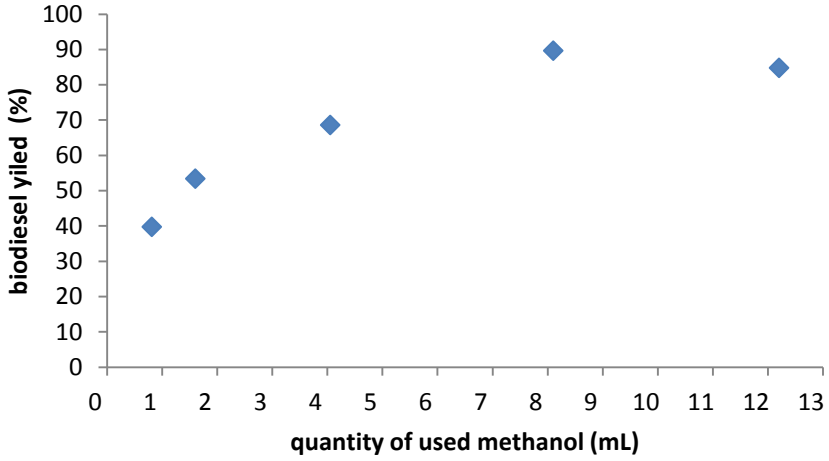


Figure 17. Effect of the oleic acid / methanol molar ratio on the biodiesel yield. (Reaction parameters: 4h, 90°C, 10% IL)

### 5.1.4 Catalyst amount

The amount of catalyst also plays important role in esterification reaction. The varying amount of catalyst [BMIM]$HSO_4$ 2.5; 5; 7.5; 10; 12.5 wt% (wt% =$m_{IL}/m_{oleic\ acid}$) was studied in this work at the following conditions: oleic acid/methanol molar ratio 1/10 during 4h and constant temperature 90°C (Appendix B, Table B1.4). Experimental results are presented in Figure 18. With the increasing amount of catalyst in the reaction, the reaction rate becomes significantly higher. However, when the dosage of catalyst exceeded a certain value, the reaction rate showed no further increase with the rise in the amount of IL catalyst, and might even have decreased.

The plot graph of biodiesel yield dependence on ionic liquid percentage is presented below. According to the plot the minimum biodiesel yield was obtained with 2.5wt% with 85.0% of yield and gradually increased reaching 89.7% of yield when using 10% of ionic liquid. After reaching this point, there was observed decreasing at 12.5 wt% with 85.9% yield. Therefore, the optimum amount of catalyst for esterification reaction was considered as 10%.

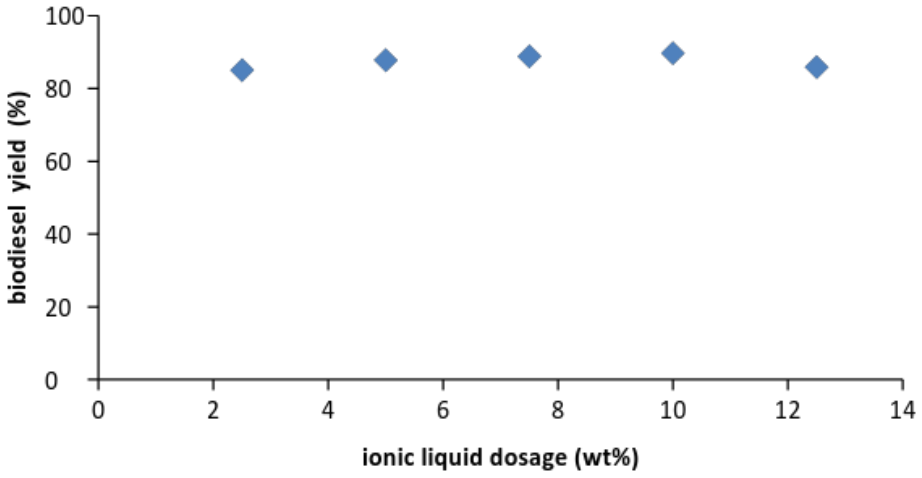


Figure 18. Biodiesel yield vs Ionic Liquid amount. (Reaction parameters: 4h, 90°C, 1/10 Oleic acid/methanol molar ratio)

### 5.2 Biodiesel characterization through FAMEs analysis

The GC analysis has been the most widely used method for the analysis of biodiesel due to its generally higher accuracy in quantifying components. Each peak corresponds to a FAME content of biodiesel by comparing their retention times to those of known standards (Table 7). All FAMEs present in the obtained biodiesel samples were identified by comparing retention times of the experimental chromatograms with the retention times of the same compounds present in the Supelco standard mixture (37 Component FAME Mix) analysis using the same method and equipment.

There are some peaks that do not correspond to any of the standards used, and thus cannot be positively identified based on retention time. Each peak does not necessarily represent just one compound. Since FAMEs are the main components of biodiesel, individual peak identification was focused on these chemical species.

In Figure 19 is presented, as an example, the experimental chromatogram obtained with one of the parameter optimization analysis: (time: 4 hr; temperature: 80˚C; Oleic Acid/methanol=1:2

and 10% IL). The software allowed for automatic integration of the peaks. In all the GC integration analysis was used a minimum chromatographic area of 6000 and a signal/noise =5

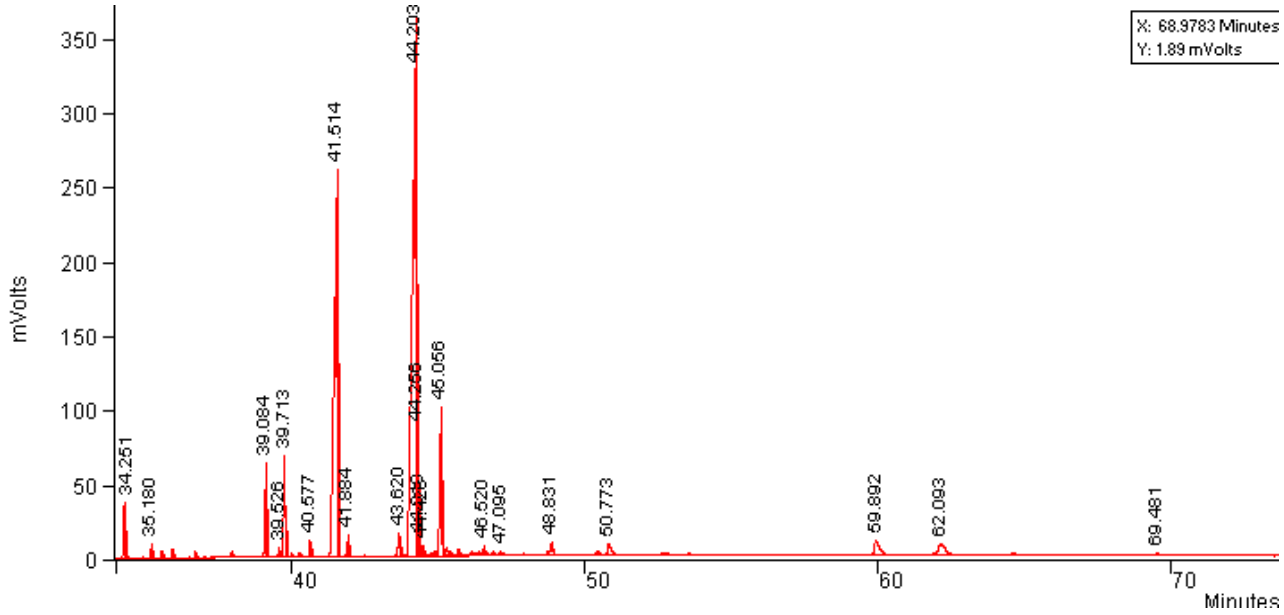


Figure 19. Chromatogram of the sample used as an example obtained by GC. (Reaction parameters: 4h, 80°C,10% IL, oleic 1/2 acid/methanol molar ratio).

According to the figure, the major peak at 44.203 min contains 2 FAMEs which represents oleic (C18:1n9c) and elaidic (C18:1n9t acid methyl ester and , although the retention time of the standard is 43.910 min, it is slightly lower, than that on the corresponding peak in the biodiesel chromatograph. The peak at 45.056 min also contains 2 FAMEs Linoleic acid methyl ester (C18:2n6c) and Lenoleaidic acid methyl ester (C18:2n6t) and at 41.514 min appears heptadecanoic acid methyl ester (internal standard).

Once the peak areas were obtained, the concentration of each methyl ester was calculated using the equation (3) in section 4.2.4. The total concentration was obtained from the sum of the areas of the identified methyl esters. [48]

The FAMEs content in all the analyzed samples was, as explained before, carried out qualitatively using the chromatographic areas and quantitatively by the internal standard method using the heptadecanoate acid methyl ester. Both analyses (%Area and %m/m) are, for this example, presented in Table 7.

Table 7. Identified FAMEs compounds present in the biodiesel sample using the Varian GC with operating reaction conditions mentioned above.

| | Components | Time(min) | Area (counted) % | Area (composition) % | % m/m |
|---|---|---|---|---|---|
| 1 | C14:0 (Myristic) | 34.251 | 117550 | 2,59 | 1,13 |
| 2 | C14:1 (Myristoleic) | 35.180 | 27539 | 0,61 | 0,27 |
| 3 | Not identified | 35.519 | 12856 | 0,28 | 0,12 |
| 4 | Not identified | 35.886 | 16806 | 0,37 | 0,16 |
| 5 | C15:0 (Pentadecanoic) | 36.677 | 11418 | 0,25 | 0,11 |
| 6 | C15:1 (cis-10-Pentadecenoic) | 37.912 | 10894 | 0,24 | 0,10 |
| 7 | C16:0 (Palmitic) | 39.084 | 228236 | 5,02 | 2,20 |
| 8 | C16:1 (Palmitoleic) | 39.526 | 20069 | 0,44 | 0,19 |
| 9 | Not identified | 39.713 | 233475 | 5,14 | 2,25 |
| 10 | Not identified | 39.952 | 7523 | 0,17 | 0,07 |
| 11 | Not identified | 40.577 | 34781 | 0,77 | 0,33 |
| 12 | C17:0 (Heptadecanoic) | 41.514 | 2084867 | 45,86 | 20,07 |
| 13 | C17:1 (cis-10-Heptadecenoic) | 41.884 | 49796 | 1,10 | 0,48 |
| 14 | C18:0 (Stearic) | 43.620 | 70783 | 1,56 | 0,68 |
| 15/16 | C18:1n9c (Oleic)/ C18:1n9t (Elaidic) | 44.203 | 2608080 | 57,37 | 25,11 |
| 17 | Not identified | 44.256 | 49057 | 1,08 | 0,47 |
| 18 | Not identified | 44.318 | 15993 | 0,35 | 0,15 |
| 19 | Not identified | 44.428 | 18208 | 0,40 | 0,18 |
| 20/21 | C18:2n6c (Linoleic)/ C18:2n6t (Linolelaidic) | 45.056 | 430232 | 9,46 | 4,14 |
| 22 | Not identified | 45.251 | 16553 | 0,36 | 0,16 |
| 23 | Not identified | 45.368 | 13783 | 0,30 | 0,13 |
| 24 | C18:3n6 (γ-Linolenic) | 45.642 | 15019 | 0,33 | 0,14 |
| 25 | Not identified | 46.105 | 7967 | 0,18 | 0,08 |
| 26 | C18:3n3 (α-Linolenic) | 46.350 | 8659 | 0,19 | 0,08 |
| 27 | Not identified | 46.520 | 21457 | 0,47 | 0,21 |
| 28 | Not identified | 46.844 | 11150 | 0,25 | 0,11 |
| 29 | Not identified | 47.095 | 20553 | 0,45 | 0,20 |
| 30 | C20:0 (Arachidic) | 47.884 | 7011 | 0,15 | 0,07 |
| 31 | C20:1n9 (cis-11-Eicosenoic) | 48.831 | 30562 | 0,67 | 0,29 |
| 32 | C20:2 (cis-11,14-Eicosadienoic) | 50.379 | 14906 | 0,33 | 0,14 |
| 33 | Not identified | 50.773 | 68779 | 1,51 | 0,66 |
| 34 | C20:3n3 (cis-11,14,17-Eicosatrienoic) | 52.597 | 7512 | 0,17 | 0,07 |
| 35 | Not identified | 53.512 | 11310 | 0,25 | 0,11 |
| 36 | Not identified | 57.351 | 6213 | 0,14 | 0,06 |
| 37 | C22:2 (cis-13,16-Docosadienoic) | 59.892 | 124281 | 2,73 | 1,20 |
| 38 | C23:0 (Tricosanoic) | 62.093 | 141851 | 3,12 | 1,37 |
| 39 | Not identified | 64.548 | 18551 | 0,41 | 0,18 |
| 40 | Not identified | 66.979 | 9677 | 0,21 | 0,09 |
| 41 | C24:0 (Lignoceric) | --- | --- | --- | --- |
| 42 | C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic) /C24:1n9 (Nervonic) | 69.481 | 26695 | 0,59 | 0,26 |
| | ***Total area without EI*** | | ***4545785*** | ***100*** | ***43,8*** |
| | ***Total FAMEs area %*** | | ***3951093*** | ***87,20*** | ***38,0*** |

According to analysis 42 compounds were identified, of which 21 are FAMEs.

This result was used to calculate the methyl oleate content expressed in %m/m and areas of components of the free fatty acid in biodiesel. The tables represent the qualitative % of methyl esters areas and quantitative methods using an internal standard solution methyl esters weight (%m/m) for all studied parameters: 1) reaction time 2) reaction temperature 3) Oleic Acid/Methanol molar ratio 4) ionic liquid percentage.

Table 8. Calculated FAME areas (%) and %m/m for optimized reaction time parameter

| Reaction parameter | Experiment value | Area of FAMEs (%) | % m/m |
|---|---|---|---|
| reaction time | 1 | 86.8 | 42.2 |
| reaction time | 2 | 76.6 | 28.1 |
| reaction time | 3 | 85.3 | 36.5 |
| reaction time | 4 | 89.9 | 40.4 |
| reaction time | 6 | 85.1 | 37.5 |
| Average | | 84.7 | 36.9 |

Table 9. Calculated FAME areas (%) and %m/m for optimized temperature parameter

| Reaction parameter | Experiment value | Area of FAMEs (%) | % m/m |
|---|---|---|---|
| temperature | $60^{O}C$ | 93.0 | 46.4 |
| temperature | $70^{O}C$ | 91.7 | 38.9 |
| temperature | $80^{O}C$ | 84.9 | 38.0 |
| temperature | $90^{O}C$ | 93.5 | 54.5 |
| temperature | $100^{O}C$ | 89.7 | 43.3 |
| temperature | $110^{O}C$ | 90.6 | 40.4 |
| Average | | 90.6 | 43.6 |

Analyzing FAME content of the experimental chromatogram obtained with oleic acid/methanol parameter optimization analysis - time: 4 hr; temperature: 90˚C; Oleic Acid/methanol=1:5 and 10% IL, an experimental error has occurred.

According to the results obtained from quantitative analysis (Table 10), the total %m/m amount of methyl esters is more than the total area of all compounds, which can not be.

Table 10. Calculated FAME areas (%) and %m/m for optimized molar ratio parameter

| Reaction parameter | Experiment value | Area of FAMEs (%) | % m/m |
|---|---|---|---|
| molar ratio | 1/1 | 85.9 | 36.0 |
| molar ratio | 1/2 | 87.2 | 38.2 |
| molar ratio | 1/5 | 26.2 | 34.2 |
| molar ratio | 1/10 | 91.7 | 51.2 |
| molar ratio | 1/15 | 20.0 | 8.5 |
| Average | | 62.2 | 33.6 |

Table 11. Calculated FAME areas (%) and %m/m for optimized IL% parameter

| Reaction parameter | Experiment value | Area of FAMEs (%) | % m/m |
|---|---|---|---|
| IL amount | 2.5%wt | 87.3 | 47.6 |
| IL amount | 5%wt | 94.4 | 46.9 |
| IL amount | 7.5%wt | 94.8 | 61.2 |
| IL amount | 10%wt | 92.7 | 51.8 |
| IL amount | 12.5%wt | 96.0 | 41.7 |
| Average | | 93.0 | 49.8 |

The figures below represent the percentages of analyzed FAMEs for optimized reaction parameters.

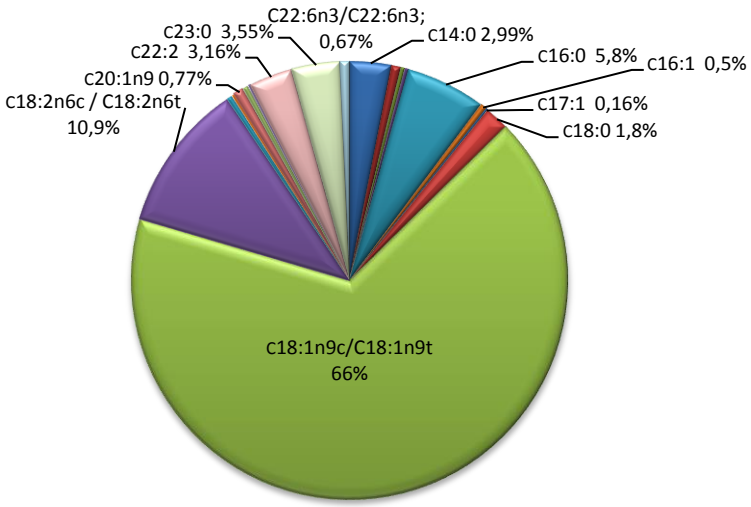


Figure 20. % of FAMEs. Effect of reaction time (Reaction parameters: 4h, 80$^{O}$C, Oleic acid/methanol molar ratio 1/2, 10% of IL)

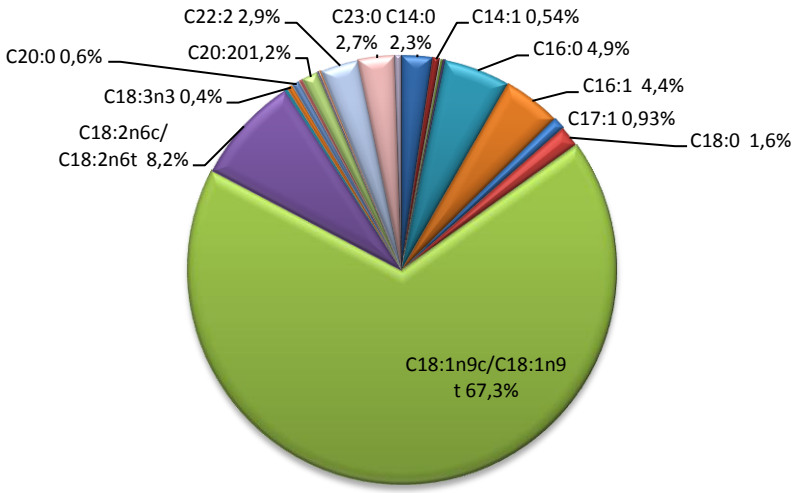


Figure 21. % of FAMEs. Effect of reaction temperature (Reaction parameters: 4h, 90$^{O}$C, Oleic acid/methanol molar ratio 1/2, 10% of IL)

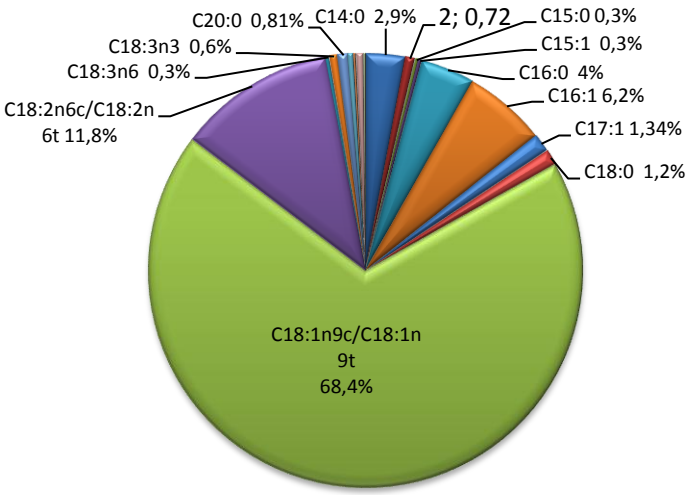


Figure 22. % of FAMEs. Effect of molar ratio (Reaction parameters: 4h, 90$^{O}$C, Oleic acid/methanol molar ratio 1/10, 10% of IL)

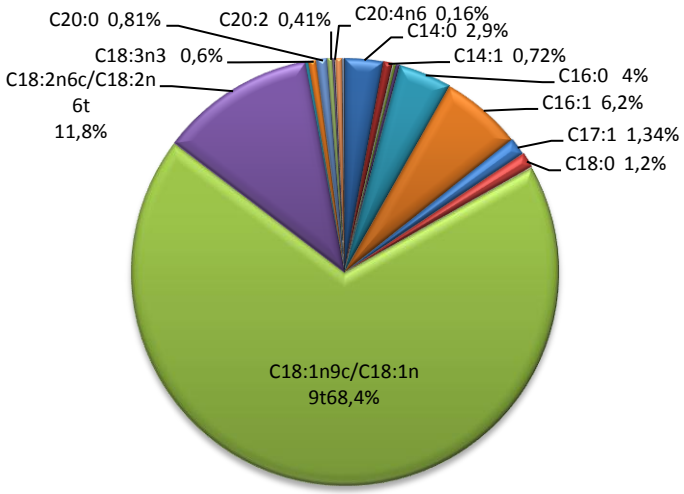


Figure 23. % of FAMEs. Effect of ionic liquid percentage (Reaction parameters: 4h, 90$^{O}$C, Oleic acid/methanol molar ratio 1/10, 10% of IL)

As it can be seen from the circular plots, the major components are C18:1n9c (Oleic)/C18:1n9t (Elaidic) and C18:2n6c (Linoleic)/C18:2n6t (Lenoleaidic) acid methyl esters.

All analyzed FAMEs percentages for optimized reaction parameters (reaction time, temperature, oleic acid/methanol molar ratio, IL amount) are presented in Appendix C, Table C1.1

# 6. Conclusions and future work

## 6. 1 Conclusions

The influence of different reaction variables on the biodiesel yield was studied using BMIM[$HSO_4$] ionic liquid as a catalyst. The investigation of the esterification of oleic acid parameters with this ionic liquid was conducted to generate the necessary information for the design of processes for obtaining high yield biodiesel. This study included the method development for analyzing the biodiesel samples using a gas chromatography.

Based on experimental results, the increasing of reaction time from 1h to 6h increased the yield of reaction from 36.3% to 53.9%.

There was experimented five reactions with various amount of ionic liquid (2.5%; 5%; 7.5%; 10%; 12.5% )with constant temperature and reaction time. The yield of the product increased from 2.5% to 10% from 85.0% to 89.7% of biodiesel yield, but there was observed sharp decrease later.

Raising operation temperature of the reaction from 60$^{o}$C to 110$^{o}$C increase the conversion from 45.6 % up to 54.4%. At 90$^{o}$C the biodiesel yield reached 53.4% of reaction conversion.

At oleic acid/methanol ratio from 1/1 to 1/10, the yield of produced biodiesel increased, however at higher ratio (1/15), there was not observed an increasing of the yield of produced biodiesel.

Analyzing FAMEs content of produced biodiesel samples, the major areas corresponds to C18:1n9c (Oleic)/C18:1n9t (Elaidic) and C18:2n6c (Linoleic)/C18:2n6t (Lenoleaidic) acid methyl esters.

Consequently, according to studied parameters, an optimum reaction condition was established as : 90$^{o}$C, 4h reaction time, 10%wt of ionic liquid and 1/10 oleic acid/methanol molar ratio.

## 6.2 Suggestions for future work

According to the study in this thesis work, there are some further important studies that need to be investigated.

In this work in order to find more optimum conditions for esterification reaction, the main reaction parameters which affect to the biodiesel conversion has been studied and satisfactory results were achieved. However, more studies have to be done to improve the reaction conditions. Further investigations of effect of reaction time on biodiesel yield: increasing reaction time might give more satisfactory results. Studying the oleic acid/methanol molar ratio, increasing molar ratio from 1/5 to 1/10, there was not observed any separation after centrifugation (see Figure 24). But after passing ~3-4 days the layers separated, and the biodiesel conversion values changed. The same problem was observed studying the effect of ionic liquid percentage. So it is important to wait at least 1 week to obtain separation.

a) 1/5 Oleic Acid/Methanol molar ratio, 4h, 90$^{o}$C

b) 1/10 Oleic Acid/Methanol molar ratio, 4h, 90$^{o}$C

Figure 24. Comparison results after centrifugation

During qualitative and quantitative analysis of produced biodiesel samples for oleic acid/methanol molar ratio parameter, there was observed, that the percentage of identified FAMEs content (62%) considerably differs from another three analyzed parameters (reaction time 84.7%. temperature 90.6% and %IL 93.0%). The oleic acid/methanol molar ratio can be studied more precisely. In order to compare results, other ionic liquids can be studied. Also reaction without catalyst can be experimented to compare biodiesel yield with and without catalyst.

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# Appendix A Titration values

## Appendix A1 Reaction time

Table A1.1 Titration data and obtained acid number and biodiesel yield

| Conditions | Initial acidity of AO | Final Acidity mgKOH/g | Conversion (%) | Concentration of KOH/MeOH solution |
|---|---|---|---|---|
| T=80$^{o}$C , t=1h, 10% IL, AO/MeOH 1/2 | 184.3 | 117.5 | 36.26 | 0.08285 |
| T=80$^{o}$C , t=2h, 10% IL, AO/MeOH 1/2 | 184.3 | 111.1 | 39.69 | 0.08285 |
| T=80$^{o}$C , t=3h, 10% IL, AO/MeOH 1/2 | 184.3 | 102.6 | 44.32 | 0.08285 |
| T=80$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 184.3 | 95.4 | 48.24 | 0.08285 |
| T=80$^{o}$C , t=6h, 10% IL, AO/MeOH 1/2 | 184.3 | 84.7 | 53.95 | 0.08285 |

# Appendix A2 Reaction Temperature

Table A2.1 Acid number data with variation of temperature

| Conditions | Initial acidity of AO | Final Acidity mgKOH/g | Conversion (%) | Concentration of KOH/MeOH solution |
|---|---|---|---|---|
| T=60$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 184.3 | 105.8 | 45.63 | 0.08285 |
| T=70$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 184.3 | 101.0 | 48.07 | 0.08285 |
| T=80$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 194.6 | 96.3 | 50.49 | 0.07885 |
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 194.6 | 90.6 | 53.44 | 0.07885 |
| T=100$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 194.6 | 90.4 | 53.52 | 0.07885 |
| T=110$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 194.6 | 88.0 | 54.50 | 0.07885 |

# Appendix A3 Molar Ratio

Table A3.1 Titration values of oleic acid/methanol molar ratio reaction products

| Conditions | Initial acidity of AO | Final Acidity mgKOH/g | Conversion (%) | Concentration of KOH/MeOH solution |
|---|---|---|---|---|
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/1 | 194.6 | 117.1 | 39.79 | 0.07885 |
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/2 | 194.6 | 90.6 | 53.44 | 0.07885 |
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/5 | 194.6 | 61.0 | 69.64 | 0.07885 |
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/10 | 194.6 | 20.1 | 88.69 | 0.07885 |
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/15 | 194.6 | 29.5 | 84.82 | 0.07885 |

# Appendix A4 Ionic liquid amount

Table A4.1 Titration values of ionic liquid amonut reaction products

| Conditions | Initial acidity of AO | Final Acidity mgKOH/g | Conversion (%) | Concentration of KOH/MeOH solution |
|---|---|---|---|---|
| T=90$^{o}$C , t=4h, 2.5% IL, AO/MeOH 1/10 | 194.6 | 29.1 | 85.03 | 0.07814 |
| T=90$^{o}$C , t=4h, 5% IL, AO/MeOH 1/10 | 194.6 | 21.4 | 88.00 | 0.07814 |
| T=90$^{o}$C , t=4h, 7.5% IL, AO/MeOH 1/10 | 194.6 | 21.7 | 88.84 | 0.07814 |
| T=90$^{o}$C , t=4h, 10% IL, AO/MeOH 1/10 | 194.6 | 20.1 | 89.69 | 0.07814 |
| T=90$^{o}$C , t=4h, 12.5% IL, AO/MeOH 1/10 | 194.6 | 27.5 | 85.88 | 0.07814 |

# Appendix B Optimization of biodiesel production

## Appendix B1 Reaction time

**Table B1.1.** Operating conditions and obtained yield for biodiesel production using [BMIM]$HSO_4$ ionic liquid as catalyst.

| Run | Time (h) | Temperature (°C) | Mass IL (g) | Mass OA (g) | Volume MeOH (mL) | Biodiesel yield (%) | AO acidity |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 80 | 0.5662 | 5.5711 | 1.6 | 36.26 | 184.3 |
| 2 | 2 | 80 | 0.5652 | 5.5919 | 1.6 | 39.69 | 184.3 |
| 3 | 3 | 80 | 0.5606 | 5.6689 | 1.6 | 44.32 | 184.3 |
| 4 | 4 | 80 | 0.5695 | 5.5492 | 1.6 | 48.24 | 184.3 |
| 5 | 6 | 80 | 0.5687 | 5.5190 | 1.6 | 53.95 | 184.3 |

## Appendix B2 Reaction Temperature

**Table B2.1.** Operating conditions set of reaction in variation of temperature.

| Run | Time (h) | Temperature (°C) | Mass IL (g) | Mass OA (g) | Volume MeOH (mL) | Biodiesel yield (%) | AO acidity |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 60 | 0.5681 | 5.6270 | 1.6 | 45.63 | 184.3 |
| 2 | 4 | 70 | 0.5675 | 5.6517 | 1.6 | 48.07 | 184.3 |
| 3 | 4 | 80 | 0.5632 | 5.6386 | 1.6 | 50.49 | 194.6 |
| 4 | 4 | 90 | 0.5612 | 5.6922 | 1.6 | 53.44 | 194.6 |
| 5 | 4 | 100 | 0.5642 | 5.6819 | 1.6 | 53.52 | 194.6 |
| 6 | 4 | 110 | 0.5643 | 5.7743 | 1.6 | 54.50 | 194.6 |

# Appendix B3 Oleic acid/methanol molar ratio

Table **B3.1**. Operating conditions for oleic acid/methanol molar ratio reactions.

| Run | Time (h) | Temperature (°C) | Mass IL (g) | Mass OA (g) | Volume MeOH (mL) 1/1 | Biodiesel yield (%) | AO acidity |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 90 | 0.5655 | 5.6576 | 0.81 | 39.79 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/2** | **Biodiesel yield (%)** | **AO acidity** |
| 2 | 4 | 90 | 0.5612 | 5.6922 | 1.6 | 53.44 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/5** | **Biodiesel yield (%)** | **AO acidity** |
| 3 | 4 | 90 | 0.5628 | 5.6389 | 4 | 68.64 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/10** | **Biodiesel yield (%)** | **AO acidity** |
| 4 | 4 | 90 | 0.5623 | 5.6434 | 8.1 | 89.69 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/15** | **Biodiesel yield (%)** | **AO acidity** |
| 5 | 4 | 90 | 0.5638 | 5.6500 | 12.2 | 84.82 | 194.6 |

# Appendix B4 Catalyst amount

Table **B4.1.** Operating conditions and obtained yield for biodiesel production using [BMIM]$HSO_4$ ionic liquid as catalyst.

| Run | Time (h) | Temperature (°C) | Mass IL (g) | Mass OA (g) | Volume MeOH (mL) 1/10 | Ionic liquid dosage (wt%) | Biodiesel yield (%) | AO acidity |
|---|---|---|---|---|---|---|---|---|
| 1 | 4 | 90 | 0.1412 | 5.7207 | 8.1 | 2.5 | 85.03 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/10** | **Ionic liquid dosage (wt%)** | **Biodiesel yield (%)** | **AO acidity** |
| 2 | 4 | 90 | 0.2831 | 5.5680 | 8.1 | 5 | 88.00 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/10** | **Ionic liquid dosage (wt%)** | **Biodiesel yield (%)** | **AO acidity** |
| 3 | 4 | 90 | 0.4237 | 5.6419 | 8.1 | 7.5 | 88.84 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/10** | **Ionic liquid dosage (wt%)** | **Biodiesel yield (%)** | **AO acidity** |
| 4 | 4 | 90 | 0.5623 | 5.6434 | 8.1 | 10 | 89.69 | 194.6 |
| **Run** | **Time (h)** | **Temperature (°C)** | **Mass IL (g)** | **Mass OA (g)** | **Volume MeOH (mL) 1/10** | **Ionic liquid dosage (wt%)** | **Biodiesel yield (%)** | **AO acidity** |
| 5 | 4 | 90 | 0.7057 | 5.6719 | 8.1 | 12.5 | 85.88 | 194.6 |

# Appendix C Comparison of 37 Component FAME Standard on Four Capillary GC Columns

Table C1.1 37 FAME mix components

| Peak ID | Acid Methyl esters | Time (min) |
|---|---|---|
| 1 | C4:0 (Butryic) | 5.880 |
| 2 | C6:0 (Caproic) | 1.987 |
| 3 | C8:0 (Caprylic) | 17.305 |
| 4 | C10:0 (Capric) | 23.498 |
| 5 | C11:0 (Undecanoic) | 26.416 |
| 6 | C12:0 (Lauric) | 29.208 |
| 7 | C13:0 (Tridecanoic) | 31.876 |
| 8 | C14:0 (Myristic) | 34.433 |
| 9 | C14:1 (Myristoleic) | 35.382 |
| 10 | C15:0 (Pentadecanoic) | 36.880 |
| 11 | C15:1 (cis-10-Pentadecenoic) | 37.803 |
| 12 | C16:0 (Palmitic) | 39.232 |
| 13 | C16:1 (Palmitoleic) | 39.858 |
| 14 | C17:0 (Heptadecanoic) | 41.482 |
| 15 | C17:1 (cis-10-Heptadecenoic) | 42.093 |
| 16 | C18:0 (Stearic) | 43.652 |
| 17 | C18:1n9c (Oleic) | 44.118 |
| 18 | C18:1n9t (Elaidic) | 44.118 |
| 19 | C18:2n6c (Linoleic) | 45.149 |
| 20 | C18:2n6t (Linolelaidic) | 45.149 |
| 21 | C18:3n6 (γ-Linolenic) | 45.884 |
| 22 | C18:3n3 (α-Linolenic) | 46.721 |
| 23 | C20:0 (Arachidic) | 48.437 |
| 24 | C20:1n9 (cis-11-Eicosenoic) | 49.089 |
| 25 | C20:2 (cis-11,14-Eicosadienoic) | 50.682 |
| 26 | C20:3n6 (cis-8,11,14-Eicosatrienoic) | 51.690 |
| 27 | C20:3n3 (cis-11,14,17-Eicosatrienoic) | 52.623 |
| 28 | C20:4n6 (Arachidonic) | 53.174 |
| 29 | C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic) | 55.476 |
| 30 | C21:0 (Henicosanoic) | 52.111 |
| 31 | C22:0 (Behenic) | 55.828 |
| 32 | C22:1n9 (Erucic) | 56.922 |
| 33 | C22:2 (cis-13,16-Docosadienoic) | 59.600 |
| 34 | C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic) | 70.104 |
| 35 | C23:0 (Tricosanoic) | 61.171 |
| 36 | C24:0 (Lignoceric) | 68.147 |
| 37 | C24:1n9 (Nervonic) | 70.104 |

# Appendix C Qualitative and Quantitative analysis of FAMEs

Table C1.1 Analyzed FAMEs percentage for all optimized parameters

| Components | FAMEs percentage | | | |
|---|---|---|---|---|
| | Reaction time | Temperature | Molar ratio | IL amount |
| C14:0 (Myristic) | 2,99 | 2,28 | 2,91 | 2,91 |
| C14:1 (Myristoleic) | 0,7 | 0,54 | 0,72 | 0,72 |
| C15:0 (Pentadecanoic) | 0,29 | 0,23 | 0,26 | 0,26 |
| C15:1 (cis-10-Pentadecenoic) | 0,28 | 0,21 | 0,28 | 0,28 |
| C16:0 (Palmitic) | 5,79 | 4,96 | 4,03 | 4,03 |
| C16:1 (Palmitoleic) | 0,5 | 4,35 | 6,17 | 6,17 |
| C17:1 (cis-10-Heptadecenoic) | 0,16 | 0,93 | 1,34 | 1,34 |
| C18:0 (Stearic) | 1,79 | 1,57 | 1,16 | 1,16 |
| C18:1n9c (Oleic)/ C18:1n9t (Elaidic) | 66 | 67,31 | 68,44 | 68,44 |
| C18:2n6c (Linoleic)/ C18:2n6t (Linolelaidic) | 10,87 | 8,16 | 11,78 | 11,78 |
| C18:3n6 (γ-Linolenic) | 0,38 | 0,25 | 0,26 | 0,26 |
| C18:3n3 (α-Linolenic) | 0,22 | 0,42 | 0,6 | 0,6 |
| C20:0 (Arachidic) | --- | 0,55 | 0,81 | 0,81 |
| C20:1n9 (cis-11-Eicosenoic) | 0,77 | 0,28 | --- | --- |
| C20:2 (cis-11,14-Eicosadienoic) | 0,37 | 1,24 | 0,41 | |
| C20:3n3 (cis-11,14,17-Eicosatrienoic) | 0,19 | 0,12 | 0,16 | --- |
| C20:3n6 (cis-8,11,14-Eicosatrienoic) | --- | --- | --- | 0,41 |
| C20:4n6 (Arachidonic) | --- | 0,16 | 0,5 | 0,16 |
| C20:5n3 (cis-5,8,11,14,17-Eicosapentaenoic) | --- | 2,87 | 0,17 | |
| C22:2 (cis-13,16-Docosadienoic) | 3,16 | 2,73 | 2,91 | 0,5 |
| C23:0 (Tricosanoic) | 3,55 | --- | 0,72 | 0,17 |
| C24:0 (Lignoceric) | | 0,48 | 0,26 | 2,91 |
| C22:6n3 (cis-4,7,10,13,16,19-Docosahexaenoic) /C24:1n9 (Nervonic) | 0,67 | 2,28 | 0,28 | 0,72 |