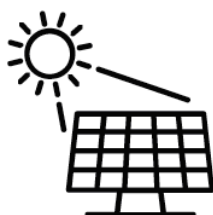




CIEEMAT`17

III Congresso  
Ibero-Americano de  
Empreendedorismo, Energia,  
Ambiente e Tecnologia:  
Livro de atas

*12 a 14 de julho de 2017*



**Título:** III Congresso Ibero-Americano de Empreendedorismo, Energia, Ambiente e Tecnologia: Livro de atas

**Editores:** Américo Vicente Leite  
Ana Isabel Pereira  
Ângela Paula Ferreira  
Artur Jorge Gonçalves  
João Paulo Almeida  
José Luis Calvo Rolle  
Manuel Joaquim Feliciano  
Orlando Manuel Soares  
Ronney Arismel Boloy

**Edição:** Instituto Politécnico de Bragança – 2017  
Campus de Santa Apolónia  
5300-253 Bragança  
Portugal

**Execução:** Orlando Manuel Soares

**ISBN:** 978-972-745-230-9

**URI:** <http://hdl.handle.net/10198/14339>

**Email:** [cieemat2017@ipb.pt](mailto:cieemat2017@ipb.pt)

**Apoios e Patrocínios:**



**Media Partner:**



50679 Study of Biodiesel Production Through Esterification Catalysed by Imidazolium-Based Ionic Liquids .....	103
50823 Performance do Processo de Digestão Anaeróbia na Valorização Energética de Resíduos de Kiwi .....	109
51200 Análise de um Sistema de Aquecimento Urbano no Campus do Instituto Politécnico de Bragança .....	115
49081 Using Zooplankton Community as Indicator of Seasonal Changes in Some Water Quality Parameters in a Meso-Eutrophic Reservoir .....	121
48831 Cassava-Processing Wastewaters: Bioremediation Potential of Immobilized <i>Chlorella vulgaris</i> (Chlorophyceae).....	127
48895 Ação dos Coagulantes Tanino, Moringa Oleifera e Cloreto Férrico Associados a Filtração Direta no Tratamento de Água em Corpos Lóticos na Região Sul do Brasil .....	131
50711 Avaliação de Impactos Ambientais na Bacia do Ribeirão Cambé em Londrina, PR, Brasil.....	135
51168 Análise do Potencial de Eutrofização Associado à Operação de uma ETAR Urbana .....	141
48308 Destinação adequada de tambores metálicos usados no Brasil – Uma análise Econômica .....	147
50687 Design of a Self-Sustainable System Based on Renewable Energy Sources for a Small Museum of Science Dissemination - The House of Silk .....	155
49099 Aprovechamiento de los Recursos Renovables e Integración de las TICs: Ejemplo Práctico de una Microrred Eléctrica .....	161
49052 Estratégia Municipal de Adaptação às Alterações Climáticas .....	167
50686 Performance Evaluation of Different Methods in the Series Resistance Estimation of Photovoltaic Modules .....	173
50571 Protótipo Acadêmico de uma Turbina Tesla com Enfoque em Reaproveitamento de Recursos .....	179
48856 Protótipo de Veículo Movido a Energias Renováveis .....	185
50269 Modelo para Prever Evolução do Preço de Commodities Minerais com o Tempo: Aplicação para o Preço das Terras-Raras .....	191
50270 Materiais Magnéticos para Motores de Carros Elétricos .....	197
50591 Máquinas de Stirling e seu Potencial para a Energia Renovável .....	203
50592 Dessalinização e sua Relevância para o Brasil em um Futuro Próximo .....	209

# Study of Biodiesel Production through Esterification Catalysed by Imidazolium-based Ionic Liquids

Alimova, I., Ribeiro, A.E., Queiroz, A.M.

Department of Chemical and Biological Technology  
School of Technology and Management,  
Polytechnic Institute of Bragança  
Campus de Santa Apolónia, 5300-253 Bragança, Portugal

Brito, P.

Department of Chemical and Biological Technology  
School of Technology and Management,  
Polytechnic Institute of Bragança  
Campus de Santa Apolónia, 5300-253 Bragança, Portugal  
paulo@ipb.pt

**Abstract**—Biodiesel is an alternative diesel fuel which is industrially produced from vegetable oils and animal fats, by transesterification reactions. Thus, currently most commercial biodiesel is produced from oils, using alkaline catalysts. On the other hand, conventional mineral acid catalysts like sulfuric acid, are commonly used for catalyzing esterification reactions of fatty acids which also produce biodiesel. However, Ionic Liquids (ILs) offer an alternative solution to classical homogeneous catalysts, because it can be recycled and reused in subsequent runs after recovery steps. An IL is a molten salt consisting of a cation and an anion, with low melting temperature. In this study, a Brønsted acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO<sub>4</sub>]) was used as a catalyst in the esterification of oleic acid with methanol into biodiesel. The effect of different operation parameters such as oleic acid to methanol molar ratio, amount of catalyst, reaction temperature, and reaction time were tested. The optimal conditions for esterification of oleic acid were experimentally determined at 1/10 for oleic acid/methanol molar ratio, 2.5 %wt for the amount of catalyst, a reaction time of 4 h and reaction temperature of 90°C. The Fatty Acid Methyl Esters (FAMES) content was analyzed using Gas Chromatography.

**Keywords**— *biodiesel, optimization, esterification, ionic liquids*

## I. INTRODUCTION

### A. Biodiesel

Biodiesel is a renewable, biodegradable, non-toxic, sulfur-free, and environmentally clean alternative diesel fuel, which 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 diesel engines, so engines do not have to be dedicated for biodiesel [1]. Comparing to diesel fuels, biodiesel fuels show advantages in terms of sulfur content, flash point, aromatic content and biodegradability. Biodiesel contribute also with lower emissions than petroleum diesel, and do not contribute to a rise of the net concentration of carbon dioxide in the atmosphere, leading to a decreasing of intensity in greenhouse effects in global climate [2].

Biodiesel is usually produced by a transesterification reaction, by which the triglycerides present in the fat materials react with alcohols, in the presence of a catalyst, to produce

fatty acid alkyl esters. Glycerol is produced as a byproduct of this transesterification process. The most common alcohol used in biodiesel production is methanol, so biodiesel is typically constituted by a mix of fatty acid methyl esters (FAMES) [3]. The transesterification reaction occurs according to the chemical equation represented in Fig. 1.

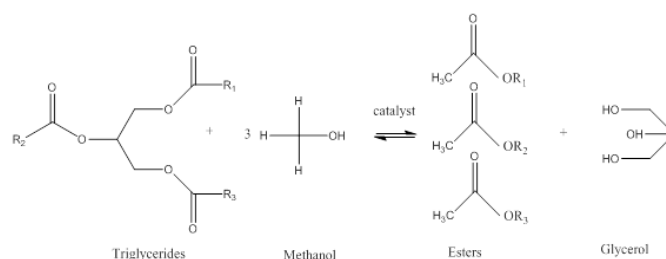


Fig. 1. Biodiesel synthesis by transesterification process from vegetable oils with methanol [4].

However for highly acidic vegetable oils, namely waste vegetable oils (WVOs), it is necessary to treat the raw materials in order to reduce its excessive acidity, which may introduce serious operational problems in the downstream processes. Thus, a previous esterification step of the free fatty acids present in the oils is required, which is usually catalyzed by conventional mineral acids, such as sulfuric acid. An esterification reaction occurs when a carboxylic acid (the fatty acid) reacts with an alcohol (usually methanol) to produce an ester (biodiesel) and water. Therefore, the main objective of the present work is to study the possibility of replacing classical catalysts typically used in esterification reactions, by an acidic ionic liquid [BMIM][HSO<sub>4</sub>], using oleic acid as a model reactant.

### B. Ionic Liquids

Ionic liquids (ILs) are defined as liquid state molten salts at low temperatures (below 100°C). They are composed of organic cations and either organic or inorganic anions, and were used as solvents/catalyst for reaction [5]. 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°C [6]. According to the cations, ionic liquids are divided into four classes: quaternary

ammonium ILs, N-alkylpyridinium ILs, N-alkyl-isoquinolinium ILs, and 1-alkyl-3-methylimidazolium ILs [7].

ILs possess properties such as: very low relative volatility (i.e., close to zero), wide liquids temperature range and significantly less toxicity compared to organic solvents. Additionally, they can be colorless, non-flammable, and show high catalytic activity, low viscosity, potential recyclability, being also easily manipulated and environmentally friendly. Moreover, they can be made miscible or immiscible with organic solvents and water. Thus, ILs which are regarded as green solvents, have received worldwide attention in several application fields including catalysis, electrochemistry, separation, and inorganic nanomaterials [8].

The most interesting characteristic of ILs 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 [8]. Besides the use as solvents, ILs can be also used as sole catalysts in biodiesel production processes [9-10], either by esterification or transesterification paths. For these applications, Brønsted acidic ILs reveal to be highly efficient catalysts.

Specifically, imidazolium based ILs, due to its inherent ionic patterns, low pressure and ability of self-organization in different states, are the most studied IL species. This kind of ionic liquids have been 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 [11-13].

The particular IL studied in this work is the acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO<sub>4</sub>]), whose chemical structure is presented in Fig. 2.

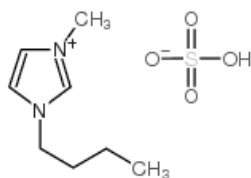


Fig. 2. Brønsted acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO<sub>4</sub>]) chemical structure.

## II. MATERIALS AND METHODS

### A. Materials

- Ionic liquid (1-butyl-3-methylimidazolium hydrogen sulfate), [BMIM]HSO<sub>4</sub> ≥94.5%, Sigma Aldrich (Switzerland);
- Oleic acid, 65-88% Ph. Eur, Sigma Aldrich (Belgium);
- Methanol, Panreac for HPLC (99.9%);
- pH indicator phenolphthalein;
- Diethyl ether, Panreac (Spain);
- Absolute ethanol, Fisher Scientific (UK);

- 37 Component FAME Mix, Supelco.

### B. Esterification Reactions

The esterification was carried out in a 100 mL glass reactor with continuous stirring, connected to a reflux condenser and a thermometer. The calculated amounts of “oleic acid” (which is in fact a mix of fatty acids containing a large content: 65-88%wt, of oleic acid) and ionic liquid were mixed in the reactor, which was then immersed into a bath (water bath or paraffin, depending on the temperature) heated to the desired temperature. Then a specified quantity of methanol was added to the mix, which was continuously stirred at 300 rpm using a magnetic stir-bar. Each reaction test was carried out at an indicated temperature, time, oleic acid/methanol molar ratio and ionic liquid weight percentage in relation to the oleic acid sample weight.

After reaction reached the desired time, it was stopped; the reactor was then removed from the bath, and cooled to room temperature. The two phases formed (biodiesel light phase and aqueous heavy phase) were allowed to separate by decantation. Afterwards, the two phases were further separated by centrifugation during 20 minutes at 3000 rpm. The biodiesel light phase sample was recovered and analyzed for the determination of the reaction yield by volumetric titration, and qualitative and quantitative FAMES (Fatty Acid Methyl Esters) content by gas chromatography.

### C. Reaction Yield

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 (EN 14104:2008 [14]). A solution of 1:1 diethyl ether/ethanol (v/v) was used as solvent for volumetric titration, and phenolphthalein was used as the indicator.

The acid value (AV) of biodiesel was calculated by:

$$AV = \frac{V \times C_{KOH} \times M_W}{m_{biodiesel}} \quad (1)$$

where,

$V$  – Volume of KOH standard solution needed to titrate biodiesel sample (mL);

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

$M_W$  – molecular weight of KOH (56.1 g/mol);

$m_{biodiesel}$  – weight of biodiesel sample (g).

The biodiesel conversion was calculated using the following equation:

$$\text{Production Yield, } Y(\%) = \frac{AV_i - AV_f}{AV_i} \times 100 \quad (2)$$

where,

$AV_i$  – acidity of oleic acid (initial) (mgKOH/g<sub>oleic acid</sub>);

$AV_f$  – acidity of sample (after reaction) (mgKOH/g<sub>biodiesel</sub>).

#### D. Gas Chromatography

The FAME content in all samples was determined using gas chromatography (GC). All analyses were carried out on a Varian 3800 GC equipment, equipped with a Supelcowax 10 column (30m×0.25mm×0.25µm) with flame ionization detector (FID). The injector temperature was set to 250°C. Injector mode fixed with split 1:20, with total running time, 85 min. The oven temperature program was previously optimized and set as: temperature held 50°C for 2 min and then increased with a 4°C/min rate until reaching 220°C.

Each sample chromatogram was compared with the 37 FAME mix Supelco Sigma standard solution chromatogram (see Fig. 3), for identification of the peak associated to each FAME present in the sample.

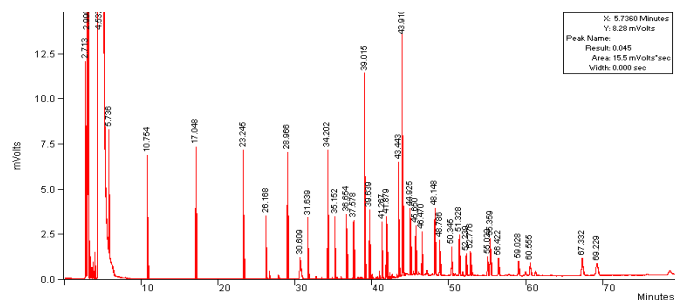


Fig. 3. Supelco 37 Component FAME Mix chromatogram using the Supelcowax 10 Column.

Therefore, by comparing obtained results with Supelco 37 Component FAME mix, all 37 FAME compounds were identified and quantified by relating the respective peak areas, using:

$$\%FAME_i = \frac{A_i}{\sum A_{FAMES}} \times 100 \quad (3)$$

where,

$A_i$  – area of the component  $i$  peak;

$\sum A_{FAMES}$  – is the total area of peaks identified as FAMES.

### III. RESULTS

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 (°C); 3) oleic acid /methanol molar ratio 4) ionic liquid amount (%wt).

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°C, with oleic acid/methanol molar ratios ranging from 1/1; 1/2; 1/5; 1/10; 1/15, for different percentages (2.5; 5; 7.5; 10; 12.5%wt) of [BMIM]HSO<sub>4</sub> ionic liquid.

#### A. Reaction Time

The reaction time was studied within the range between 1h and 6h, for a reaction temperature of 80°C. Experimental results presented in Fig. 4 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 with the rising of the reaction time. However, as the yield increasing rate is relatively low, it is assumed an optimal value around 4h.

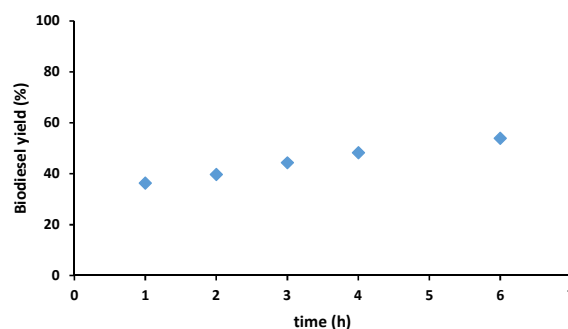


Fig. 4. Effect of the reaction time on the biodiesel yield (80°C, oleic acid/methanol molar ratio 1/2, 10% IL).

#### B. Reaction Temperature

In the following set of experiments the reaction yield was studied using a temperature range from 60°C to 110°C, using a reaction time of 4h. Increase in reaction temperature speeds up the reaction rate, and therefore increases the product yield. So, the results obtained clearly show that an increasing of temperature influences the biodiesel yield (see Fig. 5). As it can be seen from experimental results the conversion gradually increases with the temperature rise, and after reaching 90°C remains at an approximately stable position. Further increasing of temperature (100 and 110°C) does not lead to significant rising in biodiesel yield, indicating that the reaction is close to equilibrium. As a consequence, it can be considered 90°C as an optimal temperature.

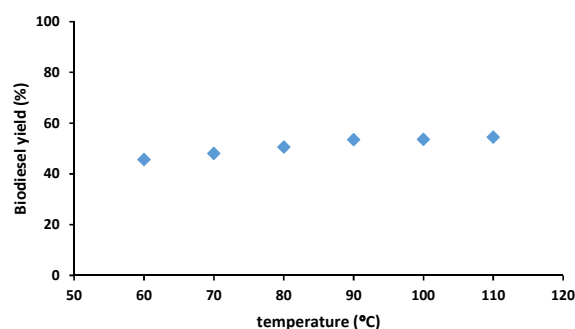


Fig. 5. Effect of the reaction temperature on the biodiesel yield conversion. (4h, oleic acid/methanol molar ratio 1/2, 10% IL).

#### C. 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°C, with a reaction time of 4h, and using oleic acid/methanol molar ratios of 1/1, 1/2, 1/5, 1/10 and 1/15. The obtained experimental results are presented in Fig. 6. Biodiesel yield at reaction time, 4h and 90°C, significantly rise with increasing methanol concentration. For lower molar ratios, higher values result in higher biodiesel conversions until a

maximum point is achieved at 89.7%, using oleic acid/methanol molar ratio of 1/10. Therefore, according to the experimental results, the optimal molar ratio of methanol to oleic acid is considered to be 1/10.

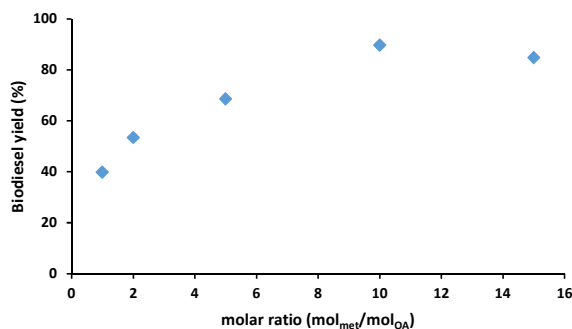


Fig. 6. Effect of the oleic acid(OA)/methanol molar ratio on the biodiesel yield. (4h, 90°C, 10% IL).

#### D. Catalyst amount

Varying amounts of catalyst [BMIM]HSO<sub>4</sub>: 2.5; 5; 7.5; 10; 12.5%wt (%wt =  $m_{IL}/m_{oleic\_acid} \times 100$ ) were studied at the following conditions: oleic acid/methanol molar ratio 1/10, during 4h, at constant temperature 90°C. Experimental results are presented in Fig. 7. With the increasing amount of catalyst, the reaction rate becomes higher. However, when the quantity of catalyst exceeds a certain value, the reaction rate showed no further increase with the rise of the amount of IL catalyst, and even show a slight decrease.

According to the results, the minimum reaction yield is obtained with 2.5%wt (85.0%) and gradually increases reaching 89.7% of yield when using 10% of ionic liquid. Afterwards it is observed a decrease for 12.5%wt with 85.9% yield. Therefore, the optimal amount of catalyst for the esterification reaction is considered as 10%.

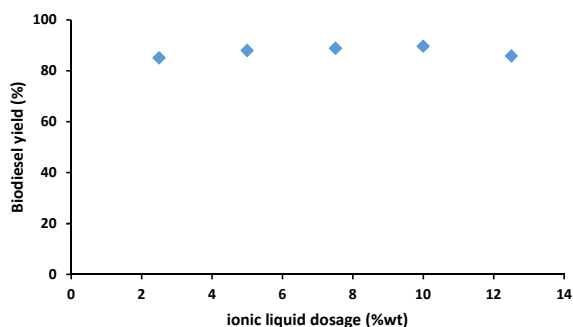


Fig. 7. Effect of the ionic liquid amount (%wt) on the biodiesel yield. (4h, 90°C, oleic acid/methanol molar ratio 1/10).

#### E. Gas Chromatography Analysis

All FAMES present in the biodiesel samples were identified by comparing the retention times of each sample chromatogram 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.

Some peaks do not correspond to any of the standards, and thus cannot be positively identified based on the retention times. On the other hand, 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. Fig. 8 represents an example, corresponding to the experimental chromatogram obtained for a specific set of conditions.

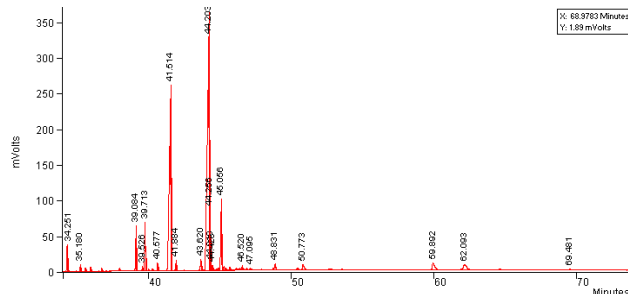


Fig. 8. Gas chromatogram of the sample used as an example. (4h, 80°C, 10% IL, oleic acid/methanol molar ratio 1/2).

According to the Fig. 8, the major peak which appears at 44.203min is associated to 2 FAMES, referring to the isomers oleic (C18:1n9c) and elaidic (C18:1n9t) acid methyl esters. Although the retention time of the corresponding standard is 43.910 min, which is slightly lower, the exit order of the sequence of FAMES, the relative higher size of the peak which is consistent for all the analyzed samples, and the expected larger quantities of oleic acid FAME in the biodiesel samples, supports the attribution of this peak to the oleic acid FAME. The peak at 45.056min also refers to two FAMES: the isomers linoleic acid methyl ester (C18:2n6c) and lenoleaidic acid methyl ester (C18:2n6t). At 41.514 min it appears a large peak referring to an internal standard added to the sample: heptadecanoic acid methyl ester.

Once the peak areas were obtained, the relative content of each methyl ester in the samples was calculated using eq. 3. The total weight quantities of FAMES were considered proportional to the sum of the areas of the identified methyl esters.

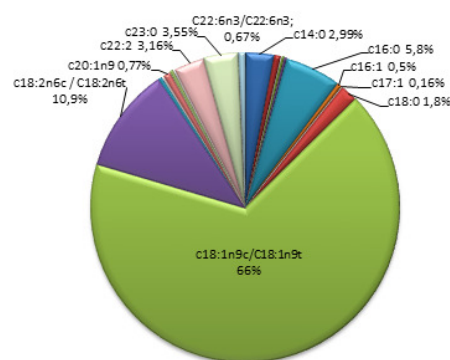


Fig. 9. Biodiesel FAME content(%wt). (4h, 80°C, 10% IL, oleic acid/methanol molar ratio 1/2).



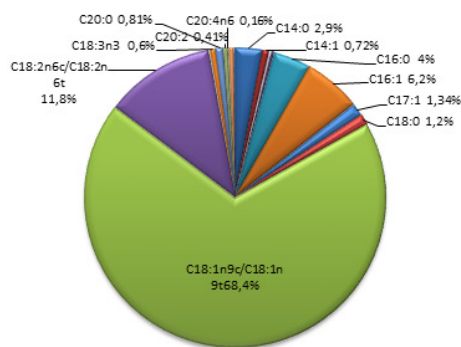


Fig. 10. Biodiesel FAME content(%wt). (4h, 90°C, 10% IL, oleic acid/methanol molar ratio 1/10).

Figs 9 and 10 represent the relative contents of FAMES present in biodiesel samples obtained for selected sets of reactional conditions. 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.

#### IV. CONCLUSIONS

The influence of different reaction variables on the biodiesel yield was studied using BMIM[HSO<sub>4</sub>] 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. However, further increasing can lead to a rise of the yield.

There were tested five reactions with various amount of ionic liquid (2.5%; 5%; 7.5%; 10%; 12.5%) with constant temperature and reaction time. The reaction yield increased from 85.0% to 89.7%, but there was observed a decrease for the higher value (12.5%).

Rising operation temperature of the reaction from 60°C to 110°C increase the reaction yield from 45.6% up to 54.5%. At 90°C the biodiesel yield reached 53.4%.

At oleic acid/methanol ratio from 1/1 to 1/10, the yield of biodiesel produced increased, but decreased for the higher ratio (1/15).

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, optimal reaction conditions were established as: temperature, 90°C, reaction time, 4h, ionic liquid amount, 10%wt, and oleic acid/methanol molar ratio, 1/10.

#### REFERENCES

- [1] M.E. Tat., and J.H. Van Gerpen, "Physical properties and composition detection of biodiesel-diesel fuel blends," The Society for engineering in agricultural, food and biological systems, An ASAE Meeting Presentation, pp. 2-11, 2002.
- [2] A.C. Ahmia, F. Danane, R. Bessah, and I. Boumesbah, "Raw material for biodiesel production. Valorization of used edible oil," *Revue des Energies Renouvelables*, vol. 17, pp. 335-343, 2014.
- [3] S.K. Hoekman, A. Broch, C. Robbins, E. Cenicerros, and M. Natarajan, "Review of biodiesel composition, properties, and specifications," *Renewable and Sustainable Energy Reviews*, vol. 16, pp. 143-169, 2012.
- [4] Z. Ullah, M.A. Bustam, and Z. Man, "Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst," *Renewable Energy*, vol. 77, pp. 521-526, 2015.
- [5] F. Guo, Z. Fang, X. Tian, Y. Long, and L. Jiang, "One-step production of biodiesel from Jatropha oil with high-acid value in ionic liquids," *Bioresource Technology Journal*, vol. 102, pp. 6469-6472, 2011.
- [6] P.M. Bollin, "Production of fatty acid methyl esters in Lewis acidic ionic liquids", Master Thesis, University of Toledo, 2011.
- [7] E.A. Visser, J.G. Huddleston, J.D. Holbrey, W.M. Reichert, R.P. Swatloski, and R.D. Rogers. "Hydrophobic n-alkyl-N-isoquinolinium salts: ionic liquids and low melting solids", *ACS Symposium Series*, vol. 975, pp. 362-380, 2009.
- [8] L. Andreani, and J.D. Rocha, "Use of ionic liquids in biodiesel production: a review", *Brazilian Journal of Chemical Engineering*, vol. 29, pp. 1-13, 2012.
- [9] A.H.M. Fauzi, and N.A.S.Amin, "An overview of ionic liquids as solvents in biodiesel synthesis," *Renewable and Sustainable Energy Reviews*, vol. 16, pp. 5770-5786, 2012.
- [10] Z.I. Ishak, N.A. Sairi, Y. Alias, M.K.T. Aroua, and R. Yusoff, "A review of ionic liquids as catalysts for transesterification reactions of biodiesel and glycerol carbonate production," *Catalysis Reviews*, vol. 59(1), pp. 44-93, 2017.
- [11] V.N. Emelyanenko, S.P. Verevkin, and A. Heintz, "Imidazolium-based ionic liquids. 1-methyl imidazolium nitrate: thermochemical measurements and ab initio calculations," *The Journal of Physical Chemistry B*, vol. 113, pp. 9871-9876, 2009.
- [12] S.O. Woon, "Synthesis and applications of imidazolium-based ionic liquids and their polymer derivatives.", Doctoral Dissertation, Missouri University of Science and Technology, Paper 1958, 2012.
- [13] J. Dupont, and P.A.Z. Suarez, "Physico-chemical processes in imidazolium ionic liquids", *Physical Chemistry Chemical Physics*, vol. 8, pp. 2441-2452, 2006.
- [14] CEN - European Committee for Standardization, "EN 14214:2008 - Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods," 2008.