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PRODUCTION AND CHARACTERIZATION OF BIODIESEL CATALYSED BY 1-BUTYL-3-METHYLIMIDAZOLIUM HYDROGEN SULFATE

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Thesis presented to the School of Technology and Management of the Polytechnic Institute of Bragança to the fulfillment of the requirements for the Master of Science Degree in Chemical Engineering, in the scope of the double degree programme with the Federal University of Technology of Paraná

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ABSTRACT

Biodiesel is a fuel generated from renewable resources with the ability to replace diesel in combustion engines. In the current scenario, its production is carried out through the esterification of free fatty acids (FFA) or the transesterification of triglycerides, always associated to catalysts, being acidic and basic respectively. The present study evaluates the influence of the application of 1-butyl-3-methylimidazolium hydrogen sulphate ionic liquid (IL), [BMIM]HSO_4, in the catalysis of the transesterification reaction of a simulated oil by the incorporation of oleic acid (OA) into the waste cooking oil in proportions of 20 and 40%wt. The operation parameters of oil/methanol molar ratio (1:20 and 1:40 mol/mol) and reaction time (4 and 8h) were studied by applying a Response Surface Methodology (RSM) using an experimental planning of Total Factorial 2^3, with the conversion of the simulated oil and the FAME content in the produced biodiesel being selected as the responses for this analysis. It is concluded that the factors of greater influence in the production of biodiesel were the incorporation of OA and the reaction time for both responses. Using a fixed catalyst load of 10%wt and a reaction temperature of 65 °C, optimum conditions for conversion were determined to be 20%wt OA incorporation, 1:20 oil/MeOH molar ratio and reaction time of 8h, leading to a conversion of 87.8%. For the FAME content the optimum condition was estimated at 40%wt OA incorporation, oil/MeOH molar ratio of 1:20 and reaction time of 8h, with a FAME content response of 37.6%wt. The optimum condition for both responses was determined through the RSM, and it is characterized by 37.3%wt OA incorporation, oil/MeOH molar ratio of 1:20 and reaction time of 8h, leading to a conversion of 82.2% and a FAME content of 35.6%wt. The kinetic studies showed that the esterification reaction of oleic acid can be modeled as a third order reaction with activation energy of 52.2 kJ/mol, and was significantly influenced by the temperature and molar ratio of oil/alcohol. It was possible to determine that with an oil/MeOH molar ratio of 1:25 the reaction reaches its optimum and that increasing the temperature the reaction conversion increases. The methodology of recovery of the ionic liquid proposed is adequate because it has the capacity to recover the IL with high purity. After five reaction/recovery cycles, the conversion efficiency falls from 93.4% to 86.9% and the FAME content decreases from 18.4%wt to 11.5%wt. In conclusion, the ionic liquid [BMIM]HSO_4 was not able to promote the transesterification reaction of the simulated oil but presented promising results for the esterification reaction and for a treatment of oils with high acidity.

Keywords: Production of biodiesel; Waste cooking oil; Ionic liquids; Response Surface Methodology; Recovery and reuse.

RESUMO

O biodiesel é um combustível gerado a partir de recursos renováveis com a capacidade de substituir o diesel em motores de combustão. No cenário atual a sua produção é realizada através da esterificação de ácidos gordos livres (AGL) ou a transesterificação de triglicerídeos, sempre associados a catalisadores, sendo ácidos e básicos, respetivamente. Neste estudo avalia a influência da aplicação do líquido iónico (LI) 1-butil-3-metilimidazólio hidrogenossulfato, $[BMIM]HSO_4$, na catálise da reação de transesterificação de um óleo simulado pela incorporação de ácido oleico (AO) ao óleo alimentar usado em proporções de 20 e 40 % em massa. Os parâmetros de produção, razão molar de óleo/metanol (1:20 e 1:40 mol/mol) e tempo de reação (4 e 8h), foram estudados aplicando uma Metodologia de Superfície de Resposta (MSR) a partir de um planeamento experimental de Fatorial Total 2^3, tendo a conversão do óleo simulado e o conteúdo de FAME no biodiesel produzido sido considerados como respostas para esta análise. Conclui-se que os fatores de maior influência na produção de biodiesel foram a incorporação de AO e o tempo de reação para ambas as respostas. Utilizando-se como parâmetros fixos a carga de catalisador em 10 %wt e temperatura de reação de 65 ºC, as condições ótimas para a conversão foram determinadas como sendo 20%wt de incorporação de AO, razão molar óleo/MeOH de 1:20 e tempo de reação de 8h, levando a uma conversão de 87.8%. Já para o conteúdo de FAME a condição ótima foi estimada em 40%wt de incorporação de AO, razão molar óleo/MeOH de 1:20 e tempo de reação de 8h, tendo como resposta para conteúdo de FAME 37.6%wt. A condição ótima para ambas as respostas foi determinada através da MSR, e é caracterizada pelos parâmetros de 37.3%wt de incorporação de AO, razão molar óleo/MeOH de 1:20 e tempo de reação de 8h, levando a uma conversão de 82.2% e um conteúdo de FAME de 35.6%wt. Os estudos cinéticos realizados foram conclusivos e permitiram concluir que a reação de esterificação do ácido oleico pode ser modelada como uma reação de terceira ordem, com energia de ativação de 52.2 kJ/mol, muito influenciada pela temperatura e razão molar de óleo/álcool. Foi possível determinar que a uma razão molar óleo/MeOH de 1:25 a reação atinge seu ótimo e que com o aumento da temperatura a reação sofre incremento na sua conversão. A metodologia de recuperação do líquido iónico proposta mostra-se adequada pois possui a capacidade de recuperar o LI com elevada pureza, sendo que, após cinco ciclos de reação/recuperação, a conversão cai de 93.4% para 86.9% e o conteúdo de FAME diminui de 18.4%wt para 11.5%wt. Em conclusão, o líquido iónico [BMIM]HSO_4 não foi capaz de promover a reação de transesterificação do óleo simulado mas apresentou resultados promissores para a reação de esterificação e como tratamento de óleos de elevada acidez.

Palavras-chave: Produção de biodiesel; Óleo alimentar usado; Líquidos iónicos; Metodologia de Superfície de Resposta; Recuperação e reutilização.

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NOMENCLATURE

Acronyms and symbols

A	Order of the reaction related to the oleic acid
A	Variable time in the experimental design (%)
AB	Interaction of A and B factors
AC	Interaction of A and C factors
A_{FAME}	Area of FAMEs
A_{IS}	Area of internal standard
ANOVA	Analysis of variance
ANVISA	Brazilian Health Surveillance Agency
AV	Acid Value (mg KOH/g of sample)
α	Error
b	Order of the reaction related to the methanol
B	Variable time in the experimental design (mol/mol)
BC	Interaction of B and C factors
c	Order of the reaction related to the biodiesel
C	Variable time in the experimental design (h)
C_0	Initial concentration (mol/L)
d	Order of the reaction related to the water
df	Degrees of freedon
DG	Diglycerides
DG-MG	Conversion of diglycerides into monoglycerides
E_a	Activation energy ($kJ.mol^{-1}$)
FFA	Free fatty acids
FID	Flame ionization detector
FT-IR	Fourier transform infrared spectroscopy
F-value	Value calculated to be compared in the Fisher's test
GC	Gas chromatography
GC-FID	Gas chromatograph with flame ionization detector

GL	Glycerol
ID	Identification
IL	Ionic liquid
k_0	Pre-exponential factor
k_1	Reaction rate constant for the direct reaction ($mol^{1-n}L^{n-1}min^{-1}$)
k_{-1}	Reaction rate constant for the inverse reaction ($mol^{1-n}L^{n-1}min^{-1}$)
k’	Reaction rate constant of the direct reaction including the concentration of methanol ($mol^{1-n}L^{n-1}min^{-1}$)
m	Mass (g)
MG	Monoglyceride
MG-GL	Conversion of monoglyceride to glycerol
OA	Oleic acid
p-value	Value calculated from the F-value
R	Ideal gas constant (8.314 $J.mol^{-1}. K^{-1}$)
R^2	Coefficient of determination
$R^2_{adjusted}$	Coefficient of determination adjusted
RNA-AG	Artificial neural network-genetic algorithm
RSM	Response Surface Methodology
$-r_{OA}$	Reaction rate of oleic acid ($mol.L^{-1}.min^{-1}$)
T	Time (min or h)
T	Temperature (ºC or K)
TGL	Triglycerides
TGL-DG	Conversion of triglycerides into diglycerides
UATR	Universal to Spectrum Two
V	Volume
X	Conversion (%)
WCO	Waste cooking oil

Formulas

BF_3	Boron trifluoride
$[BMIM]BF_4$	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM]Br	1-butyl-3-methylimidazolium bromide
$[BMIM]ClO_4$	1-butyl-3-methyl imidazolium perchlorate
$[BMIM]FeCl_4$	1-butyl-3-methylimidazolium tetrachloroferrite
$[BMIM]HSO_4$	1-butyl-3-methylimidazolium hydrogen sulfate
$[BSMBIM]CF_3SO_3$	3-methyl-1- (4-sulfo-butyl) -benzimidazolium trifluoromethanesulfonate
$[BSO_3HMIM]BF_4$	1-butylsulfonic-3-methylimidazolium tetrafluoroborate
$[BSO_3HMIM]HSO_4$	1-sulfobutyl-3-methylimidazolium hydrogen sulfate
$[BSO_3HMIM]HSO_4\text{-}Fe_2(SO_4)_3$	3-methyl-2- (1-sulfobutyl) -1H-imidazolium hydrogen sulfate III
$C_{18}H_{24}O_2$	Oleic acid molecular formula
$C_{19}H_{26}O_2$	Oleic acid methyl ester (biodiesel) molecular formula
CH_2OH	Methanol molecular formula
CH_3CHO	Acetaldehyde
CO	Carbon monoxide
[EPy]Br	1-ethyl piridinium bromide
$[EPy]HSO_4$	N-ethyl-pyridine hydrogen sulfate
H_2O	Water
HCHO	Formaldehyde
HCl	Hydrochloric acid
HCOOH	Formic acid
H_2SO_4	Sulfuric acid
$[HSO_3\text{-}BMIM]HSO_4$	1,4-propane sulfone
$[HSO_3\text{-}PMIM]HSO_4$	1,3-propane sulfone
KOH	Potassium hydroxide
MeOH	Methanol

$[MIM]HSO_4$	Methylimidazolium hydrogen sulfate
N_2	Nitrogen
NaCl	Sodium chloride
NO	Nitrogen monoxides
NO_x	Nitrogen oxides
O_2	Oxygen
OH	Hydroxy
$[PrMIM]HSO_4$	1-propyl-3-methylimidazolium hydrogen sulfate
$[PrSO_3HMIM][HSO_4$	1-propylsulfonate-3- methylimidazolium hydrogen sulfate
$SnCl_{2.}2H_2O$	Hydrated tin chloride
SO_x	Sulfur oxides
[TEAm]Cl	Tetraethylammonium chloride
$[TEAm]HSO_4$	Tetraethyl ammonium hydrogen sulfate

1. BACKGROUND AND OBJECTIVES

1.1 Background

The need to develop an alternative fuel to the petrochemical base took place essentially after the oil crisis in 1973 and the Gulf War in 1991. After these events the United States began developing alternative fuels based on mixtures of corn oil and cotton seed oil and their blends with pure diesel to replace imported diesel [1].

With the current consolidated environmental policies, the demand for biofuels is expected to grow steadily in the coming years. Projections show that the European Union will increase its consumption from 19.5 to 30.3 million tons between 2012 and 2020 respectively [2].

Currently, with the scarcity of underground carbon resources and the occurrence of global warming due to the high consumption of fossil fuels, the interest in alternative fuels has been growing and one of the resources that received much attention in this context was biofuels. The global potential of biodiesel production is very uncertain, but in the long term may represent a substantial proportion of the demand for transport fuels [1-3].

Researchers at the Swiss Federal Institute of Materials Science and Technology, in 2007, studied the impact of 26 biofuels and their environmental benefits and costs. Among these biofuels types, biodiesel produced from different sources was the one which showed more significant decrease relative to greenhouse gases regarding to their life cycle when compared to fossil fuels, reaching a reduction of more than 50% [4].

Biodiesel is an alternative clean-burning fuel, which is produced from fats, vegetable oils or animal fats, and the chemical structure of the molecule consists, mostly, of esters of fatty acids. When compared to petroleum diesel, its great advantages are: being produced from renewable resources, have an ecological emission profile, as well as being biodegradable and environmentally friendly. The major disadvantage is that it has a high cost of production [1,3].

Being aware of such advantages and disadvantages, the search for alternative biodiesel production is a current concern. This study focuses on the investigation of these new alternatives so that the cost of production, environmental concerns, competition with food and search for catalysts that allow greater efficiency in the production process are satisfied. In this scenario, the production of biodiesel from waste oils and the application of ionic liquids as catalysts have been applied as a possible alternative to overcome the disadvantages of the traditional production process, in order to minimize conflicts with the food industry, through the use of residual or inedible oils. On the other hand, ionic liquids can be recovered and reused, which makes the process environmentally more efficient and less expensive.

1.2 Objectives

1.2.1 Main objectives

The main objective of this work is the study of the application of an imidazolium type ionic liquid in the catalysis of esterification/transesterification reactions of mixtures of triglycerides derived from waste oils with high free fatty acids (FFA) contents.

1.2.2 Specific objectives

- Determination of the operational parameters (reaction time, reaction temperature, alcohol/oil molar ratio and catalyst dosage for the production of biodiesel based on the transesterification reaction of a waste oil, using 1-butyl-3-methylimidazolium, [BMIM]HSO_4, as catalyst;
- Evaluation of the yield of the transesterification reaction through the characterization of the biodiesel produced;
- Carry out kinetic studies to determine the activation energy of the transesterification reaction to biodiesel production;
- Proposal of alternatives for the recovery of the IL used as catalyst.

1.3 Document structure

This dissertation is composed of five chapters. This first chapter presents a background about the context in which biofuels currently fit, giving emphasis to biodiesel, as well as the proposed objectives of this study and the structure of this document.

The second chapter presents the introduction, consisting of a theoretical review of studies already done related to biodiesel production, highlighting the advantages and disadvantages of the different feedstock used, their properties, production methods and catalysts used, as well as kinetic studies of the involved reactions and recovery methods of the catalysts.

In the third chapter the experimental section is described, including materials, equipment and methodologies used in the experimental work.

The fourth chapter presents the experimental results obtained and the appropriate discussion.

Finally, the fifth chapter summarizes the main conclusions as well as the suggestions for the future works.

2. INTRODUCTION

2.1 Biodiesel

Biodiesel can be chemically defined as a mixture of alkyl esters of long chain fatty acids (FAME) that are produced from a wide range of oily materials such as vegetable oils and animal fats, obtained by the transesterification reaction of triglycerides or by reaction of esterification of free fatty acids, and can be used as an alternative fuel for diesel engines that have compression ignition [2,5,6].

2.1.1 Advantages and disadvantages of biodiesel

The properties of biodiesel and a petroleum diesel are, for the most part, similar, allowing a mixture of both in any proportions, without the need of modification of the ignition diesel engines, which maintains practical unchanged its performance [2,4,7].

To the detriment of petroleum diesel, biodiesel has some very attractive characteristics, such as the emission of lower levels of greenhouse gases because it is produced from vegetal and animal resources; it is biodegradable and its burning results in reduced levels of particulates. Biodiesel provides a reduction of emissions of SO_X, CO, hydrocarbons, soot, and particles. On the other hand, the consumption of biodiesel leads to a slight increase in NO_x emissions [5].

However, some studies have shown that fuels with a good flammability, it means, with high methyl oleate content, provide lower levels of NO, hydrocarbons, HCHO, CH_3CHO and HCOOH and also that soot formation is suppressed when exposed to burning, since biodiesel is an oxygenated fuel having an O_2 mass fraction of 10% [5].

The benefit obtained from the use of biodiesel is directly proportional to the level of this mixture with petroleum diesel applied to motors. By assessing the carbon dioxide life cycle, it is possible to detect a 78.45% reduction in overall emissions when comparing pure biodiesel to a blend of 80% petroleum diesel and 20% biodiesel, which represents a decrease in net issues by 15.66% [9].

In contrast to these data, according to the International Energy Agency, biodiesel produced with current technology is about two to three times more expensive than petrol and diesel oil [10].

2.1.2 Raw materials used in biodiesel production

Currently, the production of biodiesel implies higher costs than the production of diesel derived from petroleum, due in large part to the high cost of the raw materials used. Some studies show that the value added of the raw materials represents about 75% of the biodiesel production cost [2,7].

The biodiesel production process can use different types of raw materials as oleaginous source, which can be edible vegetable oils (soybean, repeseed and palm derivatives), inedible vegetable oils, used food oils, animal fat, and oils extracted from algae. However, all these alternatives have some advantages and disadvantages for the process, as can be seenin the Table 1 [8,12].

Table 1. Advantages and disadvantages of the different raw materials used in biodiesel production.

Feedstock	Advantages	Disadvantages
Edible oils	Do not require pre-treatment	Competition with the food market
Inedible oils	Reduced price and no competition with the food sector	Low yields because they contain free fatty acids, need to purify the final product
Waste oils	Reduced price and no competition with the food sector	High content of free fatty acids and moisture, need for pre-treatment
Animal fat	High availability at low cost	High content of free fatty acids and non-viability of the product to be used at low temperatures due to its high viscosity
Algae	Fast algae growth and high oil yield, ecologically friendly and year-round availability.	Necessary upstream and downstream processes (dehydration of algae, extraction of oil and purification of the product).

Source: Nurfiltri *et al.* (2013) ; Sun *et al.* (2017) [8,12].

The main disadvantage of raw materials with a high content of free fatty acids is that they lead to saponification reactions during the production process if they are not subjected to previous treatments. The saponification reaction drastically reduces the yield of biodiesel production, hindering the production process [8]. Table 2 presents the comparison of the distribution of fatty acids in different feedstock from vegetable oils, animal fats, and other fats.

Table 2. Quantification (in weight %) of fatty acids from different feedstock.

Feedstock	**Fatty acid distribution (%)**							
	C14:0	**C16:0**	**C16:1**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**Others**
Chicken fat	-	19.82	3.06	6.09	37.62	31.59	1.45	0.37
Tallow	3.10	23.80	4.70	12.70	47.20	2.60	0.80	5.10
Pork lard	1.30	23.50	2.60	13.50	41.70	10.70	-	6.70
Rapeseed oil	-	3.49	-	0.85	64.40	22.30	8.23	0.73
Sunflower oil	-	5.40	0.10	2.90	28.70	72.90	-	0.00
Soybean oil	-	10.58	-	4.76	22.52	52.34	8.19	1.61
Yellow grease	2.43	23.24	3.79	12.96	44.32	6.07	0.67	5.62
Brown grease	1.66	22.83	3.13	12.54	42.36	12.09	0.82	4.48

Source: Nurfiltri *et al.* (2013) [8].

In general, both fat and oils are essentially triglycerides. The distinction between fats and oils refers to the physical state of each at room temperature. The fats are solid and the oils are usually liquid. However, there are hydrogenated oils that acquire a solid aspect at this temperature [12].

Fats are usually classified into two categories, whose differentiation occurs by the level of free fatty acids in the respective composition. The yellow fat is produced from a triglyceride source which undergoes a heating process, having free fatty acids (FFA's) limit of 15%. When fat exceeds this value, it is called brown fat [12].

In Table 2 it can be seen that the most abundant acids in the composition of these materials are oleic acid, referring to C18:1 and linoleic acid, represented by C18:2.

2.1.2.1 Waste oils

A residual oil is defined as any vegetable oil suitable for food that has been exposed to frying or cooking processes. During this procedure the oil is heated at temperatures between 160 and 190 °C and, because of this, changes occur in its physical properties, such as increase of viscosity and specific heat, as well as changes in surface tension and coloration in response to the degradation of triglycerides and formation of other compounds [11,12].

During the culinary process, the oil is subjected to thermolytic, oxidative and hydrolytic reactions. The first reaction occurs in the absence of oxygen at elevated temperatures, producing alkanes, alkenes, ketones, carbon monoxide and carbon dioxide from the fatty acids. The oxidative effect is derived from the reaction of dissolved oxygen in the oil with the unsaturated alkylglycerols, having as derivatives saturated and unsaturated aldehyde, hydrocarbons, ketones, alcohols, acids, esters, among other compounds. Considering the possible reactions, the hydrolytic reactions are the most relevant for the subsequent biodiesel production process, since they lead to the increase of free fatty acids (FFAs), monoglycerides and diglycerides in the oil composition [13].

Refined oils have a low amount of FFAs, around 0.5%, while in residual oils this value is around 2 to 7%. The Health Surveillance Agency of Brazil (ANVISA) establishes that oils that exceed the limit of 0.9% of FFAs are unfit for consumption and should be discarded. In this way, they become excellent alternatives as raw material for the production of biodiesel [13].

The reuse of waste oils for the production of biodiesel has the potential to reduce the cost of production by approximately 45%, even taking into account the cost increase with the pre-treatments necessary for the reduction of water content and FFAs, besides having relevance for reducing environmental impacts [11,13].

For biodiesel production, oils having a moisture content above 0.5% and an FFA content higher than 2.5% must undergo previous treatments, as these will have a major influence on the production of biodiesel, resulting in possible saponification reactions when using traditional basic catalysts, and therefore decreasing the yield of the reaction. Most of the time, these pre-treatments are steam injection, neutralization, vacuum filtration and vacuum evaporation of the residual oil. For other cases, there is also the heating process, which in brief consists in raising the oil temperature to 100 °C for fifteen minutes with continuous stirring. There is also the possibility of a chemical treatment process, where magnesium sulfate is used as a water absorber. However, these treatments can lead to the decomposition of the oil and the formation of unwanted products, reducing the formation of esters [11,12].

2.1.3 Biodiesel properties

Some physical and chemical properties of biodiesel obtained from different vegetable oils, as well as for biodiesel and gas oil, are presented in the Table 3. It is explicit that the various types of biodiesel have viscosities and densities approximate to those of diesel, and their lower heating value values are slightly smaller, having high cetane number and flash points [5].

Table 3. Properties of the diesel, gas oil and biodiesel from different feedstock.

Vegetable oils methyl ester	Kinematic viscosity (mm^2/s)	Cetane number	Lower heating value (MJ/ton)	Flash Point (ºC)	Density (g/L)	Sulfur (wt%)
Peanut	4.9[a]	54	33.6	176	0.883	-
Soybean	4.5[a]	45	33.5	178	0.885	-
Babassu	3.6[a]	63	31.8	127	0.879	-
Palm	5.7[a]	62	33.5	164	0.880	-
Sunflower	4.6[a]	29	33.5	183	0.860	-
Repessed	4.2[b]	51-59.7	32.8	-	0.882[d]	-
Used repessed	9.48	53	36.7	192	0.895	0.002
Used corn oil	6.23[c]	63.9	42.3	166	0.884	0.0013
Diesel fuel	12-3.5[b]	51	35.5	-	0.830-0.840[d]	-
JIS-2D A (gas oil)	2.8[c]	58	42.7	59	0.833	0.05

[a] 37.8 °C; [b] 40 °C; [c] 30 °C; [d] 15 °C;
Source: Adapted from Fukuda *et al.* (2001) [5].

Each of these properties presented in Table 3 represents a parameter of fundamental importance in determining biodiesel quality. The kinematic viscosity is the representation of flow resistance under gravity, indicating the completion stage of the biodiesel synthesis reaction. The cetane number of a diesel fuel molecule is strictly related to the combustion rate and the level of compression required for the ignition. The lower heating value indicates the amount of heat released by the combustion reaction of a sample of the fuel, and the flash point is the ignition temperature of the fuel [15].

2.1.4 Biodiesel production methods

Oils and fats from plant and animal sources are a promising alternative for the replacement of the use of fossil fuels. However, its high viscosity becomes a problem for the ignition of motors, and it is necessary to consider mechanical changes to their use to be feasible [5,16].

That way, new methodologies are currently being studied to reduce the viscosity of these materials rich in triglycerides. There are some processing alternatives to the production of biodiesel such as the transesterification reaction, esterification reaction, pyrolysis, and microemulsification. The transesterification reaction has been favorable for obtaining triglycerides derivatives with characteristics similar to petroleum diesel and an esterification reaction is a good option for the conversion of free fatty acids (FFA) present in the used oils into alkyl esters of fatty acids [5,16].

2.1.4.1 Esterification

The esterification reaction is a condensation reaction between carboxylic acids and alcohols resulting in esters. In the case of biodiesel production, these carboxylic acids are free fatty acids [16].

Figure 1 depicts the esterification reaction where the carboxylic acid reacts with the alcohol, giving ester and water.

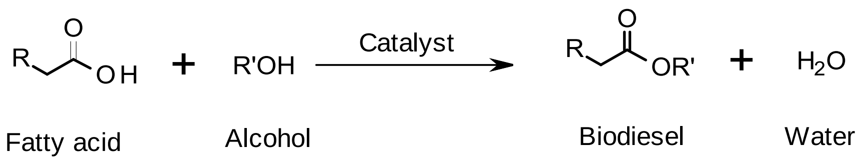


Figure 1. Scheme of the reaction of esterification.
Source: Adapted from Andreani e Rocha (2012) [16].

The mechanism proposed by Fischer in which the esterification reaction of the carboxylic acids occurs is tetrahedral. The reaction takes place in five steps, as shown in Figure 2. In the first step, the oxygen of the carbonyl group belonging to the carboxylic acid is captured by the acid catalyst. In the next step, the carbonyl carbon undergoes attack by the nucleophile, thus generating a tetrahedral intermediate. In the third step, there is the transfer of a proton from the alcohol to the OH group. Subsequently, the elimination of a molecule of water takes place, leading to the formation of a protonated ester. In the last step, the proton loss and formation of the ester product occurs [17].

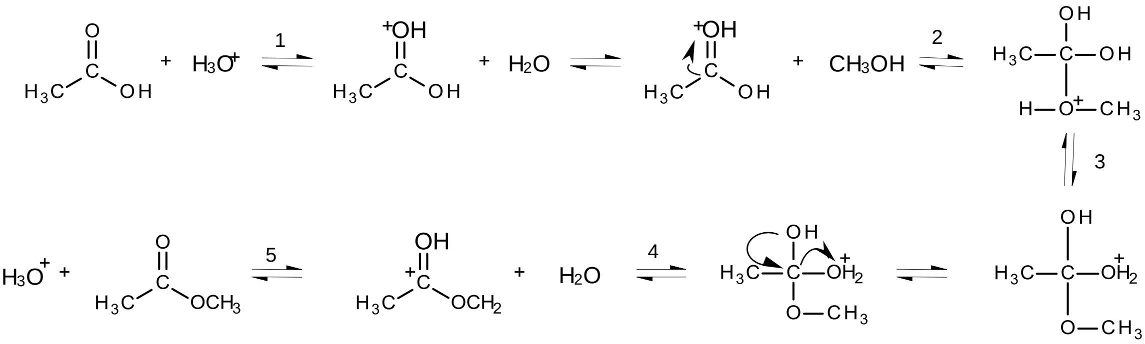


Figure 2. The mechanism proposed for the esterification reaction.
Source: Adapted from Zeng *et al.* (2012) [17].

2.1.4.2 Transesterification

The transesterification process is a sequence of three consecutive steps. In the first of these, the triglyceride is converted to a diglyceride, subsequently this product is converted to a monoglyceride and, finally, the glycerol is obtained from the conversion of the monoglyceride. Generally, for the actual conversion of oils to biodiesel, the presence of catalysts is required [16].

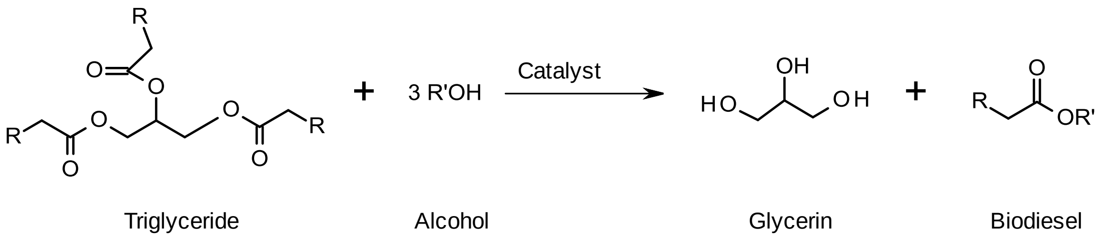


Figure 3. Scheme of the transesterification reaction.
Source: Adapted from Andreani e Rocha (2012) [16].

The alcohols that can be used in the transesterification process are methyl, ethyl, propyl, butyl, and amyl, being the most used methyl and ethyl. Methanol is widely used due to its low cost and its physicochemical properties, such as polarity and lower molecular size. As shown in Figure 3, the stoichiometric ratio between the alcohol and the triglyceride in the transesterification reaction is

3:1. However, transesterification of vegetable oils is a reversible reaction, so that the yield of the reaction depends on the displacement of the chemical balance in favor of the esters. Therefore, an excess of alcohol is generally more appropriate to increase the displacement of the equilibrium reaction for the products. In addition, it is necessary to optimize other factors, such as catalyst concentration, temperature, and agitation of the reactive environment [16].

2.1.5 Catalysts used in the production of biodiesel

The presence of catalysts for biodiesel production becomes necessary for an effective conversion, being that they vary between homogeneous, heterogeneous or enzymatic, and they can be acidic or basic [13].

The basic catalysts are widely used because they have a lower cost and high availability, being the most applied sodium hydroxide and potassium hydroxide. In addition, low amounts of alcohol are required and the reaction time is satisfactory, in the order of a few hours. However, the production process of biodiesel catalyzed by a base is very sensitive to the presence of water and FFAs; high concentrations of water lead to the hydrolysis of the triglyceride, increasing the amount of FFAs, which reacts with the catalyst, leading to the saponification reaction. The saponification reaction, in addition to causing unproductive consumption of the catalyst that would be required to catalyze the production of biodiesel, also hampers the process of purification of the final product, because the phase separation between the glycerol and the esters is inhibited during the process of washing by the formation of an emulsion. Therefore, the use of basic catalysts in oils that have high levels of FFA, such as waste oils, is very difficult, requiring pre-treatments, which makes the process slow and expensive [12,15].

The acidic catalysts are not sensitive to the FFA, which makes them great alternatives to be used in oils with high levels of acidity; sulfuric and sulphonic acids are the most common in this class. However, these catalysts lead to a reaction time up to 4000 times higher, higher alcohol/oil molar ratios, around 30-150:1, higher temperatures and can lead to corrosion of the equipment, resulting in high costs [12,15].

The great advantage of heterogeneous catalysis when compared to homogeneous catalysis is the possibility of producing in continuous, eliminating the drawbacks of by-products and the ease of separation of the products of the process. However, the reaction rate decreases due to the mass transfer resistance between the different phases [13].

Enzymatic catalysis is an alternative to the traditional methods of biodiesel production, which overcomes the disadvantages of previous catalytic systems, such as saponification reaction and corrosion of equipment. This alternative presents a lower energy cost because it only requires bland temperatures and pressures; it is easy to remove by-products and products with high purity. However, even the enzymatic reactions are highly specific and chemically clean, they require between 4 to 40 hours of reaction, the temperature is about 35 °C to 45 °C, requiring strict control of pH and temperature and especial care in the choice of solvent because of the possibility of denaturation [6,12,15].

In view of the points presented above, several alternatives that aim to overcome the problems encountered have been studied. In the literature it is possible to find researches focused on the study of heterogeneous catalysts [18,19], organic bases [20], without the presence of a catalyst using supercritical methanol [21] or supercritical ethanol [22]. In the meantime, the choice of ionic liquids (IL) have been shown to be highly promising [6,16,23,24].

Ionic liquids used in catalytic systems represent an environmentally responsible process, with the possibility of recycling and reuse, as well as being able to be used in the treatment of by-products from biodiesel production and transesterification of vegetable oils and animal fats, such as acids or bases, acidic, alkaline or enzymatic catalysts [16].

2.1.6 Ionic liquids

By definition, ionic liquids (ILs) are organic salts composed exclusively of ions, the cation being always organic, while the anion can be organic or inorganic. They are liquids at room temperature, having a melting point below 100 °C because of the large size of their molecule, the displaced charge and the difficulty in packaging. The ionic attraction present in the molecule causes the ionic liquids to present negligible vapor pressures, providing the non-emission of volatile organic compounds during their use, in addition to exceptional thermal and chemical stability. Furthermore, these compounds exhibit high catalytic activity, low viscosity, are poorly toxic, non-flammable, easily handled and have a high recyclability potential [15,22,23].

Ionic liquids have a high ability to dissolve a wide variety of compounds, being polar or nonpolar, organic, inorganic or polymeric, and this is due to their stable structure, since they have dipole-dipole, van der Waals interactions, hydrogen interactions, as well as electrostatic interactions, which makes them excellent solvents [16].

The most important characteristic of ionic liquids is the possibility of designing the molecule according to its specific application, tracing a certain set of properties such as melting point, viscosity, density, water solubility and selectivity [15,23].

In addition to the use as solvents, ionic liquids are being widely applied in a variety of catalysis, electrochemical, separation and nanotechnology processes. Since these compounds have a high price, their recycling and reuse capacity makes them highly attractive, enabling the reduction of the cost of operation. The recycling process, most of the times, occurs through distillation, solvent extraction, adsorption or the application of separation membranes [22-24].

When referring to the production of biodiesel using ionic liquids as catalysts, some studies show that the acidic character of the ionic liquid has great influence on the catalytic action of biodiesel production; this feature, described by Bronsted and Lewis, is influenced by both the cation and the anion of the molecule. Besides that, ionic liquids are capable of significantly reducing the number of purification steps in the fuel production process, since, for example, they do not require pre-treatments for the reduction of free fatty acid content or post treatment in the case of saponification, reducing the cost of their production [25,26].

Figures 4 and 5 demonstrate the proposed mechanism for biodiesel production via a basic and acidic transesterification reaction, respectively [23].

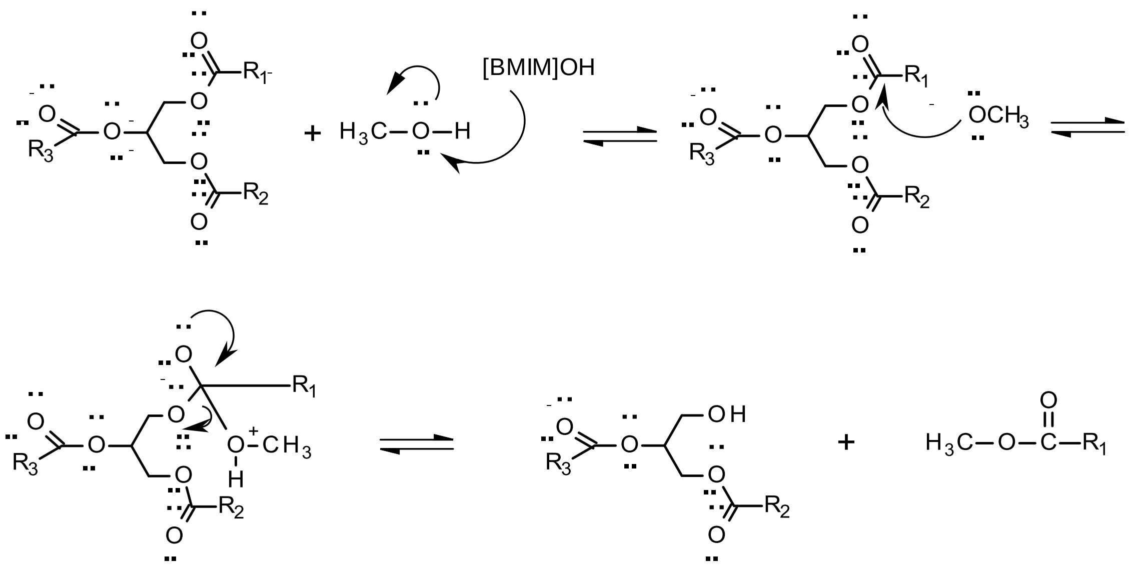


Figure 4. Proposed mechanism for transesterification reaction for the production of biodiesel catalyzed by the basic ionic liquid.
Source: Adapted from Ishak *et al.* (2017) [23].

The transesterification mechanism catalyzed by a basic ionic liquid begins with the deprotonation of the methoxide group by the ionic liquid, which being basic is negatively charged. The methoxide group, now active, attacks the carbonyl group present in the triglyceride, forming an intermediate. This intermediate is then converted to a diglyceride group, which produces methyl ester, or is reverted to the starting compound since the transesterification reaction is reversible when there is excess of alcohol [23].

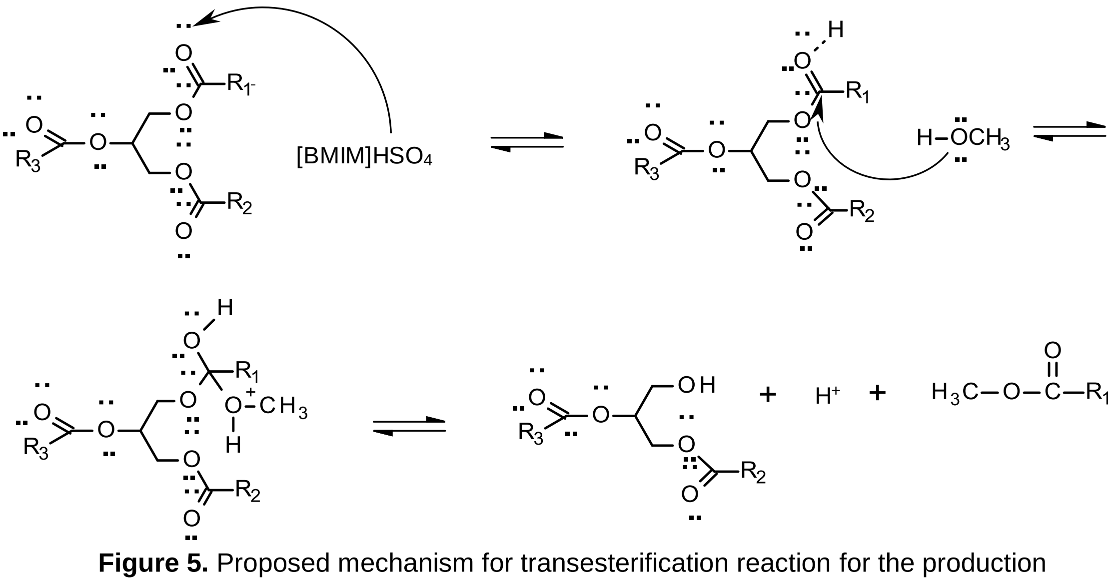


Figure 5. Proposed mechanism for transesterification reaction for the production of biodiesel catalyzed by the basic ionic liquid.
Source: Adapted from Ishak *et al.* (2017) [23].

By the same principle, the mechanism of the transesterification reaction catalyzed by an acidic ionic liquid begins with the anion yielding a proton to the carbonyl group present in the triglyceride, forming an intermediate, which in turn reacts with the methoxide group by means of a nucleophilic substitution reaction forming the diglyceride molecules, methyl ester, and one proton to catalyze the next reaction [23].

2.1.6.1 Ionic liquids applied in biodiesel production

Ionic liquids based on imidazolium have been mostly studied in catalysis for biodiesel production due to their low pressure and self-organization capability in different states, and, among these, 1-butyl-3-methylimidazolium hydrogen sulfate [BMIM]HSO_4 has been showing promising results [26].

Fauzi and Amin (2013) [30] performed a multiobjective optimization of the esterification reaction, using oleic acid and methanol, catalyzed by ionic [BMIM]HSO_4, using an Artificial Neural Network-Genetic Algorithm (ANN-GA), and varied parameters such as temperature, reaction time, molar ratio between methanol and oleic acid and the catalyst dosage. The authors determined the optimal values of these variables for both the conversion of oleic acid and the yield of methyl oleate: these conditions were defined as 87 °C, a reaction time of 5.2 hours, alcohol/oleic acid molar ratio of 9:1 and catalyst dosage of 0.06 mol. These optimal conditions allowed 80.4% of conversion of oleic acid and 81.8% yield of methyl oleate.

Li *et al.* (2014) [31] also conducted a study for the esterification reaction of oleic acid with methanol, having as variable the type of catalyst used. The researchers used seven ionic liquids as reaction accelerators, namely 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4), N-ethyl-pyridine hydrogen sulfate ([EPY]HSO_4), tetraethyl ammonium hydrogen sulfate ([TEAm]HSO_4), 1-sulfobutyl-3-methylimidazolium hydrogen sulfate ([$BHSO_3$MIM]HSO_4), 1-butyl-3-methyl imidazolium perchlorate ([BMIM]ClO_4) 1-ethyl piridinium bromide ([EPY]Br) tetraethylammonium chloride ([TEAm]Cl). The other variables were kept constant, with the alcohol/oleic acid molar ratio of 2:1, the percentage of catalyst being 10% by mass and the temperature of 80 °C. From these ILs,

$[BHSO_3MIM]HSO_4$ showed the best result for catalytic activity at a reaction time of 4 hours , giving a yield of 72.4%, followed by $[BMIM]HSO_4$ with 60%.

Fauzi and Amin (2012) [32] studied the production of biodiesel from the esterification reaction of oleic acid with methanol, using as catalyst $[BMIM]HSO_4$. The authors identified as optimum conditions for the procedure, the molar ratio of alcohol /oleic acid of 9:1, catalyst load of 3.4% by mass, reaction time of 4 hours and the reaction temperature of 90 °C, resulting in an oleic acid conversion of 84.43%. In addition, they determined that the variables that have the greatest influence in this process are the reaction temperature and the catalyst dosage.

Alimova (2016) [33] carried out a study of biodiesel production through the esterification reaction of oleic acid with methanol, using $[BMIM]HSO_4$, and having as variables reaction time, reaction temperature, methanol/oleic acid molar ratio and catalyst dosage. It was obtained as optimum operating conditions a reaction time of 4 hours and reaction temperature of 90 °C, a molar ratio alcohol/oleic acid of 10:1 and catalyst charge of 10 %wt, thus resulting in a conversion of 89.7%.

Tadevosyan (2017) [34] in a similar study on the production of biodiesel by an esterification reaction between oleic acid and methanol, also tested $[BMIM]HSO_4$ as a catalyst. The parameters used were molar ratio of alcohol/oleic acid of 10:1, a reaction temperature of 90 ºC and reaction time of 6 hours. It was obtained a conversion of 76.6% regarding to oleic acid using a catalyst dosage of 10% by mass, 83.3% conversion of oleic acid using 15% by mass of catalyst and 84.8% conversion of oleic acid for a dosage of 20% by mass of catalyst.

Ullah *et al.* (2015) [3] conducted research on the production of biodiesel from a two-step process. In the first step, an esterification reaction was carried out from waste cooking oil and methanol, catalyzed by an ionic liquid in order to decrease the acidity of this oil. In the second step, KOH was used to catalyze the transesterification reaction. Three ionic liquids were used in the first phase of the process: 1-butyl-3-methylimidazolium hydrogen sulfate ($[BMIM]HSO_4$), butylimidazolium hydrogen sulfate ($[BIM]HSO_4$) and methylimidazolium hydrogen sulfate ($[MIM]HSO_4$). The best result was obtained with, $[BMIM]HSO_4$, therefore the best conditions for this step being a catalyst concentration of 5% by mass, alcohol/oil molar ratio of 15:1, a reaction time of 60 min and the reaction temperature of 160 °C. The second phase, catalyzed transesterification using

KOH, was carried out at 60 °C, with 1% by mass of catalyst dosage and reaction time of 60 min. At the end of the two steps, the overall yield reached was 95.65%. In addition to the aforementioned researches.

Elsheikh et *al.* (2011) [35], carried out a study on the production of biodiesel from the transesterification reaction. They used crude palm oil as feedstock and investigated imidazolium-containing ionic liquids, such as [BMIM]HSO_4, [BIM]HSO_4, [MIM]HSO_4, to determine which one had the highest catalytic potential. The best results were obtained with [BMIM]HSO_4, reaching a conversion of 91.2% in the optimum conditions: 4.4% in weight of catalyst concentration, alcohol/oil molar ratio of 12:1, reaction temperature of 160 °C and reaction time of 120 min.

Li *et al.* (2014) [36] conducted research on the production of biodiesel from the transesterification reaction. They used the seed oil of *Camptotheca acuminata* in the presence of various imidazolium-based acidic liquids acting as catalysts (1-butyl-3-methylimidazolium bromide, [BMIM]Br; 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM]BF_4; 1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4; 1-butylsulfonic-3-methylimidazolium tetrafluoroborate, [BSO_3 HMIM]BF_4; 1-sulfobutyl-3-Methylimidazolium hydrogen sulfate [BSO_3HMIM] HSO_4). At a methanol/oil ratio of 6:1, a catalyst concentration of 5% in weight, temperature of 60 °C and a reaction time of 30 min, only the third best result was obtained with the IL [BMIM]HSO_4 among the five catalysts studied, presenting a conversion ratio of 38.5%.

An alternative form of biodiesel production is using algae as raw material. Sun *et al.* (2017) [11] performed the transesterification reaction using *Nannochloropsis* catalyzed by [BMIM]HSO_4. The reactor was then pressurized to 200 psi (1.38 MPa) by injecting compressed N_2 after addition of reactants in all experiments. They obtained as optimal operating conditions methanol/wet algae mass ratio of 3:1, reaction temperature of 200 °C, reaction time of 30 min and a mass ratio of algae with [BMIM]HSO_4 of 0.9, resulting in a conversion of 95.28%.

Table 4 summarizes the information discussed above.

Table 4. Summary of the experimental conditions found in the literature for biodiesel production reactions catalyzed by [BMIM]HSO_4.

Reaction	**Feedstock**	**Ratio alcohol/oil**	**Catalyst dosage (%wt)**	**Temp (°C)**	**Reaction time (h)**	**Conversion (%)**	**REF**
Esterif.	Oleic acid	9:1 molar	1.2	87	5.2	81.8 e 80.4[a]	[30]
Esterif.	Oleic acid	2:1 molar	10	80	4	60.0	[31]
Esterif.	Oleic acid	9:1 molar	3.4	90	4	84.4	[32]
Esterif.	Oleic acid	10:1 molar	10	90	4	89.7	[33]
Esterif.	Oleic acid	10:1 molar	20	90	6	84.8	[34]
Esterif./ Trans.	Wast cooking oil	15:1 molar	5.0	160	1	95.6[b]	[3]
Trans.	Crude palm oil	12:1 molar	4.4	160	2	91.2	[35]
Trans.	Oil of *Camptotheca acuminata*	6:1 molar	5.0	60	0.5	38.5	[36]
Trans.	*Nannochloropsis*	3:1 mass	0.9	200	0.5	95.3	[11]

[a] 81.8% and 80.4% for methyl oleate yield and conversion of oleic acid respectively;
[b] after esterification with IL and transesterification with KOH.

In the literature there are also some studies conducted for the production of biodiesel using FAME content to determine the conversion of the reaction.

Fran et al. (2017) [37] studied the catalytic action of four types of imidazolium ionic liquids (ILs) in the transesterification reaction of rapeseed oil: 1-propyl-3-methyl-imidazolium hydrogen sulfate ([PrMIM]HSO_4), 1-propylsulfonate-3-methylimidazolium hydrogen sulfate ([$PrSO_3HMIM$][HSO_4]), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4), and 1-butylsulfonate-3-methylimidazolium hydrogen sulfate ([BSO_3HMIM]HSO_4). The effects of molar ratio of methanol to rapeseed oil, catalyst dosage, reaction temperature and reaction time, and the deactivation of water in the catalytic activity were explored. The temperature of the reaction was varied from 90 to 140 °C in six experiments, maintaining other parameters constant, catalyst concentration of 10 %wt, 10:1 molar ratio of methanol/oil and reaction time of 5 h. The catalysts analyzed showed different catalytic activities. The catalyst [BMIM]HSO_4 presented the best results with a reaction temperature of 110 ºC, resulting in a FAME content of only 8.89%, and showing that this is the ionic liquid with the lowest catalytic activity among those studied.

Sun *et al.* (2017) [11] investigated the influence of some parameters on the production of biodiesel by in-situ transesterification of Nannochloropsis to fatty acid methyl esters catalyzed by 1-butyl-3-methylimidazolium hydrogen sulfate . Biodiesel production was studied for a range of reaction temperature of 100-200

°C, reaction time between 0-180 min and algal mass ratio with [BMIM]HSO_4 of 0.3, 0.6, 0.9, 1.2. The reaction temperature was favorable to crude biodiesel yield at the temperature ramp of 100-200 °C. The results also proved that [BMIM]HSO_4 catalyzed in situ transesterification can achieve the optimum yield in a short time of 30 min, with crude biodiesel yields also increasing with an increase in the mass ratio of [BMIM]HSO_4 to wet algae initially; however, the yield of the crude biodiesel declined somewhat after the mass ratio was above 0.9. Under these conditions the FAME conversion is around 37%.

2.1.6.2 Recovery of ionic liquid

In order to overcome the high price of the ionic liquid used in the proposed processes of biodiesel production, several methods of recycling these compounds are being researched, aiming at the conservation of the reaction yield.

Some authors have studied methods of recovering [BMIM]HSO_4 after it has been used as a catalyst in biodiesel production. Among them, Fauzi and Amin (2013) [30] proposed some alternatives to recover this catalyst. After the production of biodiesel by esterification reaction, the phases were separated, the lower one being characterized by a mixture of unreacted ionic liquid, water, and methanol and the upper phase was an organic phase, containing a biodiesel. This mixture undergoes drying, being heated overnight at 105 °C to evaporate water and alcohol. The authors performed five cycles of reaction with the catalyst, with 80.4% oleic acid conversion and 81.8% methyl oleate yield practically constant.

Tadevosyan (2017) [34], after the transesterification reaction and phase separation, proposed drying the sample in an oven for one hour at 110 °C followed by introduction into a vacuum oven at 60 °C for a period of 12 to 15 hours. There was a recovery of the catalyst 5 times, after these cycles, the reaction yield decreased from 84.8% to 77.1%.

Sun *et al.* (2017) also proposed a recycling method of [BMIM]HSO_4: posteriorly to the reaction of biodiesel production, the aqueous phase was collected after filtration of algae and then dried by vacuum over night at 60 °C. The authors recovered the ionic liquid 4 times successfully, reducing the yield for the 95.28% to 81.23%.

2.1.7 Kinetic studies

The study of kinetic parameters in the production of biodiesel, either through the esterification or transesterification reaction, is, in this context, of fundamental importance because it brings a better understanding of the relevance of the catalyst in the process. The activation energy (E_a) is the decisive variable in this analysis since it demonstrates the minimum energy required for the reaction to occur, allowing an idea of whether or not the catalyst is effective [38].

Aranda *et al.* (2008) [39] carried out studies on the reaction of esterification of palm fatty acids with methanol applying different acid catalysts. In this study, the researchers varied the parameters of catalyst concentration and reaction temperature. As a first conclusion, the compounds with the highest catalytic activity were sulfuric acid and methanesulfonic acid, and the reactions with both catalysts were modeled with the kinetics of first order. They also concluded that the activation energy of the reaction decreased as the catalyst dosage increased, obtaining, for a catalytic charge of 0.01% by mass, an activation energy of 15.05 $kJ.mol^{-1}$ for the reaction catalyzed by acid sulfuric, and 10.12 $kJ.mol^{-1}$ for the reaction catalyzed by methanesulfonic acid. The increase in catalyst dosage to 0.05% by mass decreased the E_a value to 6.53 $kJ.mol^{-1}$ and 3.775 $kJ.mol^{-1}$, respectively.

Cardoso *et al.* (2008) [40] investigated the production of biodiesel from the esterification reaction of FFAs from oleic acid in the presence of soybean oil with ethanol. The authors studied the catalytic activity of tin hydrochloride hydrate ($SnCl_2.2H_2O$) in homogeneous phase as an alternative to sulfuric acid. The authors reported that the kinetic behavior of this process is related to a first-order reaction, for an ethanol/oleic acid molar ratio of 120:1 and a temperature range of 45-75 °C was used. They also determined that the E_a for the reaction has a value of 46.69 $kJ.mol^{-1}$.

Jansri *et. al.* (2011) [41] researched the reaction between the palm oil and methanol, analyzing this process in two steps. In the first, a reaction of esterification of the FFAs catalyzed with sulfuric acid and later a reaction of transesterification of triglycerides catalyzed by sodium hydroxide. The authors determined the kinetics of both reactions, having concluded that the esterification reaction was first order, and transesterification reaction was second order. They also estimated the activation energy, varying the temperature between 55 ºC and 65 ºC, and obtained 17997 cal.mol^{-1} (75.3 kJ.mol^{-1}) for the esterification reaction. For the transesterification reaction, study for each step of the reaction was done separately: conversion of triglycerides to diglycerides (TGL-DG) 348 cal.mol^{-1} (1.45 kJ.mol^{-1}), conversion of diglycerides into monoglycerides (DG-MG) 78560 cal.mol^{-1} (328 kJ.mol^{-1}) and monoglyceride into glycerol (MG-GL) 21356 cal.mol^{-1} (89.35 kJ.mol^{-1}).

Li *et*. *al.* (2014) [36] studied the process of biodiesel production by microwave-assisted transesterification reaction from *Camptotheca acuminate* seed oil and methanol catalyzed by various acidic liquids, and the one with the highest catalytic activity was [BSO$_3$HMIM]HSO$_4$ - Fe$_2$(SO$_4$)$_3$. They performed a detailed study of the kinetic behavior of biodiesel production based on the procedure using a microwave, having a temperature range of 40 ºC to 60 ºC, stipulated that this reaction is of the first order and has an activation energy of 37.68 kJ.mol^{-1}.

Fauzi *et al.* (2014) [42] studied the reaction of esterification of oleic acid with methanol using the ionic liquid 1-butyl-3-methylimidazolium tetrachloroferrate [BMIM]FeCl$_4$ as a catalyst. They performed the reaction with methanol/oleic acid molar ratio of 22:1, catalyst dosage 1mmol, a reaction time of 3.6 h and temperature range of 40 °C to 70 °C. They concluded that the reaction follows a pseudo-first order kinetics, estimating the E$_a$ value to be 17.97 kJ.mol^{-1} and the pre-exponential factor (k$_0$) of 181.62 min^{-1}.

Neumann *et al.* (2016) [43] investigated the esterification reaction of oleic acid with ethanol, with sulfuric acid as the catalyst. The authors conclude that the kinetic behavior of the process can be described by a second order reaction, resulting in activation energy with a value of 36.62 kJ.mol^{-1} and a k$_0$ of 4.72×10^2 m^3.mol^{-1}.s^{-1}.

Kostic *et al.* (2016) [44] researched the connection of reaction of esterification of residues of plum with methanol, applying acid sulfuric as a catalyst. The authors performed variations in the reaction conditions of catalyst dosage, methanol/oil ratio and reaction temperature (40 ºC to 60 ºC). In this way, they modeled the kinetic behavior as being a first-order reaction and concluded that the activation energy of this process decreases with increasing catalyst dosage. They stated that 0.049 mol.dm^{-3} of catalyst leads to an activation energy of 13.20 kJ·mol^{-1}, while 0.172 mol.dm^{-3} of catalyst leads to an E_a of 11.55 KJ·mol^{-1}, which defined as a very small difference.

Ullah *et al.* (2017) [45] have developed studies of the reaction of transesterification of waste oils and methanol, applying as catalyst the ionic liquid 3 - methyl - 1 - (4 - sulfo - butyl) - benzimidazolium trifluoromethanesulfonate [BSMBIM]CF_3SO_3. They modeled the reaction of biodiesel production as being of the first order, ignoring the intermediates of the reaction. The temperature range was 80 °C to 140 °C, resulting in an E_a of 19.24 KJ.mol^{-1}.

Ding *et al.* (2017) [46] conducted one study with the aim of improving the efficiency of the production of biodiesel catalyzed per acid. To that used three different acid ionic liquids based on imidazolium, [MIM]HSO_4 (1-methyl imidazolium), [HSO_3-PMIM]HSO_4 (1,3-propane sulfone) and [HSO_3-BMIM]HSO_4 (1,4 propane sulfone), to catalyze the transesterification reaction of palm oil under microwave irradiation. The ionic liquids used that had the highest catalytic activity was [HSO_3-BMIM]HSO_4. The authors determined as the optimal condition a catalyst dosage of 9.17%, methanol/oil molar ratio of 11:1, microwave power of 168 W and reaction time of 6.43 h. According to the results obtained, the kinetic model of pseudo-first order is the most suitable for the process, having an activation energy of 56.12 kJ.mol^{-1}.

Roman *et al.* (2018) [46,47] carried out a study of biodiesel production through the esterification reaction of oleic acid catalyzed by [HMIM]HSO_4. The kinetic study allowed to estimate the activation energy of the esterification reaction reaching a very low value of 6.8 kJ .mol^{-1}. A set of experiments was carried out using conditions optimized for conversion: 15% by weight of catalyst dosage, a methanol/oleic acid molar ratio of 15:1, reaction time of 8h and reaction temperature varied in each experiment: 110, 100, 90, 80 and 70 °C. The order of the reaction was studied, and the researcher determined that the highest coefficient of determination for all temperatures was found for a 3rd order reaction. Table 5 summarizes the above information.

Table 5. Summary of kinetic studies found in the literature.

Feedstock	**Rection**	**Alcohol**	**Catalyst**	**T (ºC)**	**Order**	**E_a (kJ/mol)**	**REF**
Palm fatty acids	Esterif.	MeOH	CH_3SO_2OH	130-160	1	10.12 – 3.78[a]	[39]
Oleic acid	Esterif.	EtOH	$SnCl_2.2H_2O$	45-75	1	46.69	[40]
Palm oil	Esterif.	MeOH	H_2SO_4	55-65	1	75.30	[41]
	Transt		KOH		2	1.45 – 328 - 89.35[b]	
Oil of *Camptotheca acuminata*	Transt/ Microwave	MeOH	$[BSO_3HMIM]HSO_4$ - $Fe_2(SO_4)_3$	40-60	1	37.68	[36]
Oleic acid	Esterif.	MeOH	$[BMIM]FeCl_4$	40-70	1	17.97	[42]
Oleic acid	Esterif.	EtOH	H_2SO_4	75-120	2	36.62	[43]
Residues of plum	Esterif.	MeOH	H_2SO_4	40-60	1	13.20 – 11.55[a]	[44]
Waste oils	Transt.	MeOH	$[BSMBIM]CF_3SO_3$	80-140	1	19.24	[44]
Palm oil	Transt./ Microwave	MeOH	$[HSO_3$-$BMIM]HSO_4$	108	1	56.12	[46]
Oleic acid	Esterif.	MeOh	$[HMIM]HSO_4$	70-110	3	6.8	[46, 47]

[a] change in catalyst dosage; [b] TGL-DG; DG-MG; MG-GL respectively.

3. EXPERIMENTAL SECTION

3.1 Materials

The feedstocks used during the biodiesel production process were waste oil, from restaurants in the region of Bragança, Portugal, oleic acid (OA), tech 90%, obtained from ThermoFisher and 1-butyl-3-methylimidazolium hydrogen sulfate obtained from Sigma Aldrich.

The other materials used during the characterization and analysis were n-heptane (99%), anhydrous absolute ethanol and sodium sulfate anhydrous were obtained from Carlo Erba. Diethyl ether, methanol, potassium hydroxide, borax and red methyl indicator were obtained by Riedel-de-Haën. Concentrated sulfuric acid and boron trifluoride-methanol was obtained from Sigma Aldrich and hydrochloric acid (37%) obtained from Fisher Chemical. The 37 FAME mixture was purchased from Sigma Aldrich. Methyl heptadecanoate (97%) was purchased by Tokyo Chemical. The phenolphthalein indicator (99%) was obtained by Panreac.

All materials were used without further purification.

3.2 Equipment

The reactions for biodiesel production were carried out in an automatic heating plate (IKA, model C-MAG HP4), using a condenser to reflux the excess methanol present in the reaction solution.

For the phase separation of biodiesel produced, a centrifuge (SIGMA, model 2-4) was used. Drying was carried out in an oven (SCIENTIFIC, series 9000). The masses of the samples were measured with an analytical balance with a precision of ±0.0002 g (AE, model ADA 210/C).

The FAME content in biodiesel samples was evaluated in a gas chromatograph (SHIMADZU Nexis GC 2030) equipped with FID detector, an autoinjector AOC-20i and an OPTIMA BioDiesel F (30mx0.25mmx0.23µm) capillary column. The infra-red spectroscopy analysis were done using a PerkinElmer spectrometer, Spectrum Two FT-IR Performance model, using a Universal ATR accessory.

3.3 Methodology

3.3.1 Reaction

Ionic liquid, oleic acid, waste cooking oil and methanol were added, using this order and in different previously defined proportions, to a 100 mL reaction vessel. Then, the reaction vessel was immersed in a paraffin bath (2), coupled to a reflux condenser (4) and placed over an automatic heating plate with agitation (1) and automatic temperature control. An extra thermometer (3) was used to confirm the temperature inside the reaction vessel, as shown in Figure 6.

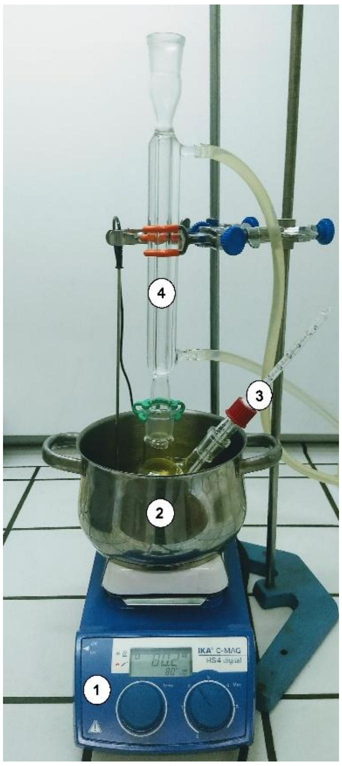


Figure 6. Experimental set up for the reaction.
1: heating plate with temperature and agitation control; 2: paraffin bath; 3: thermometer to control the reaction temperature; 4: condenser for methanol reflux.

When the predetermined reaction time was reached, the vessel was removed from the bath and immersed in cold water to stop the reaction. The mixture was transferred to centrifuge tubes and then stored in a refrigerator (4 °C) for a period of 60 h, then subjected to 20 minutes of centrifugation (3000 rpm). Using this procedure, the final product of the reaction reached a level of complete separation of phases that could be completely splitted.

Using a Pasteur pipette, the phases were separated into identified vials. Figures 7 and 8 shows the steps described.
Both phases were stored in flasks and keep into fridge awaiting for analysis.

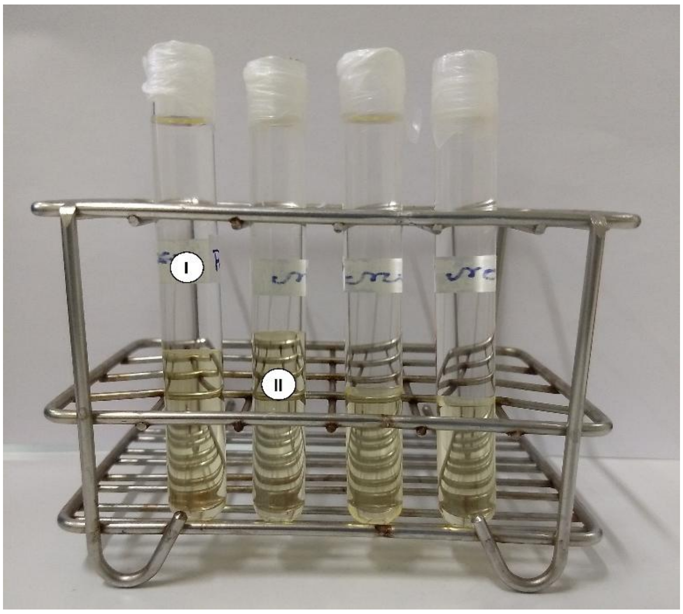


Figure 7. Phases separation. I (upper phase): aqueous phase and/or glycerin; II (lower phase): organic phase.

Figure 8. Separated phases in individual vials.

3.3.2 Experimental design

In order to estimate the optimal operating conditions, three factors were studied. Using a Design Expert 11 software, Response Surface Methodology (RSM) was employed, for the application of this methodology an experimental design was used to generate a code matrix for implementation. The Total Factorial Design 2^3, having three factors with two levels and one repetition, being: percentage of

OA incorporated (20% and 40% wt.), oil/methanol molar ratio (1:20 and 1:40) and reaction time (4 h and 8 h), as shown in Table 6. The methodology estimates that 16 runs are adequate to understand the influence of each factor on the response. The design matrix in coded and in real values is displayed in Table 7.

Table 6. Parameters and codes for Factorial Design.

Paramentes	Code	-1	1
Incorporation of OA (%wt)	A	20	40
Molar ratio oil/methanol (mol/mol)	B	1:20	1:40
Reaction time (h)	C	4	8

Table 7. Conditions applied to each run, in coded values and in experimental values.

Runs	Coded values			Experimental Values		
	A	B	C	Incorporation of OA (%)	Molar ratio oil/MeOH (mol/mol)	Reaction time (h)
1	1	1	1	40	1:40	8
2	-1	-1	1	20	1:20	8
3	1	-1	-1	40	1:20	4
4	1	-1	-1	40	1:20	4
5	-1	1	1	20	1:40	8
6	1	-1	1	40	1:20	8
7	-1	-1	-1	20	1:20	4
8	-1	-1	-1	20	1:20	4
9	-1	-1	1	20	1:20	8
10	-1	1	-1	20	1:40	4
11	1	1	-1	40	1:40	4
12	1	1	-1	40	1:40	4
13	1	-1	1	40	1:20	8
14	-1	1	1	20	1:40	8
15	1	1	1	40	1:40	8
16	-1	1	-1	20	1:40	4

Two responses were evaluated: the conversion and the FAME content.

3.3.3 Acidity and conversion measurements

The acid value was calculated to measure how much free fatty acids (FFAs) were present in the sample. This calculation was performed according to European Standard 14104/2003 [49].

After the production and separation of phases, 1 g of biodiesel sample was transferred to an Erlenmeyer using a micropipette and an analytical balance was used to measure the weight. Then, 25 mL of the solvent was added 1:1 (v/v) ethanol/diethyl ether and 5 drops of phenolphthalein and the solution was then titrated with a standard solution of potassium hydroxide.

The acid value (AV) is calculated using equation 1:

$$AV\left(\frac{mg\ KOH}{g\ biodiesel}\right) = \frac{V_{KOH} * C_{KOH} * MM_{KOH}}{m_{biodiesel}} \qquad (1)$$

Where V_{KOH} is the volume of the KOH standard solution used in the titration, in mL, C_{KOH} is the concentration of the KOH solution, in mol/L, MM_{KOH} is the molar mass of KOH (56.1 g/mol) and $m_{biodiesel}$ is the measured biodiesel mass, in g.

The conversion was estimated by comparing the initial acid value of the waste oil/OA mixture to the acid value of the final product, according to the formula expressed by equation 2:

$$X = \frac{AV_{oil/OA} - AV_{biodiesel}}{AV_{oil/OA}} \times 100 \qquad (2)$$

Where X is the conversion, in %; $AV_{oil/OA}$ is the acidity for the waste oil/OA mixture and $AV_{biodiesel}$ is the acidiy of biodiesel, both in mg_{KOH}/g_{sample}.

3.3.4 Determination of FAME content in biodiesel samples

Gas Chromatography with a Flame Ionization Detector (GC-FID) was used to measure the FAME (Fatty Acid Methyl Esters) content in biodiesel samples, in compliance with the European Standard EN14103/2003 [50].

Figure 9 shows the equipment used for performing the analysis.

Figure 9. GC-FID equipment used for FAME analysis in biodiesel samples.

After the determination of the acidity, the organic phase was subjected to a drying process using an oven at 105 ºC for 2h. The biodiesel samples were then prepared for gas chromatography analysis. Aliquots of 250 mg were transferred to 10 mL flasks and then 5 mL of methyl heptadecanoate (used as internal standard) solution with a concentration of approximately 10 mg/mL was added. Then, small quantities of anhydrous sodium sulfate were added to remove the remaining moisture present in the sample. The flask was then closed and stirred appropriately, the salt was decanted and 1 μL of the solution was withdrawn into a 2 mL vial for analysis.

The GC analysis were carried out using the following operating conditions: helium flow-rate of 1 mL/min, initial oven temperature of 50 °C maintained for 1 min, then a temperature ramp from 25 °C/min to 200 °C, and then a second ramp temperature at 3 °C/min until 230 °C. The final temperature was maintained for 23 min, for a total running time of 40 min. The injector was operated with a temperature of 250 °C and a split ratio of 1:25. The detector temperature was 250 °C.

The identification of each FAME was done by comparing the retention times of the Supelco 37 FAME compound mix analysis obtained in the GC Shimadzu system with the retention times in two other analysis of FAMEs mixtures published by two different manufacturers. The first one is a 16 FAME mix analysis published by Macherey-Nagel [51] using the same column OPTIMA BioDiesel F (see Figure 10) and the second one is a 37 compounds mixture which is the 37 FAME compound mix analysis published by Supelco [52] using a DB-Wax column (see Figure 11).

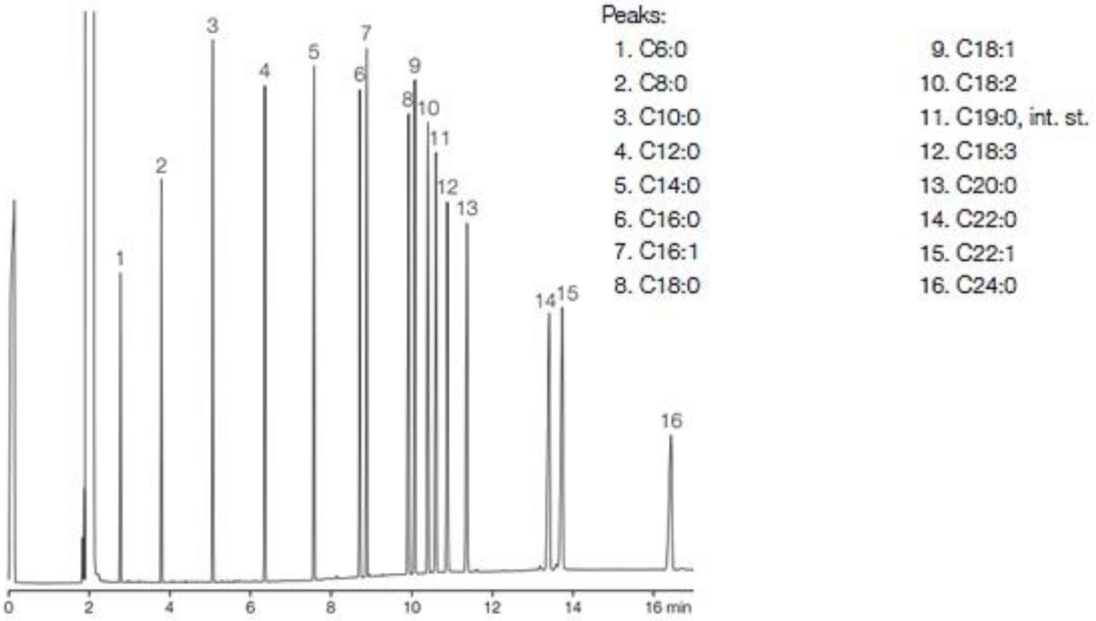


Figure 10. Chromatogram for 16 component FAME mix from OPTIMA BioDiesel F column. Source: MACHEREY-NAGEL [51].

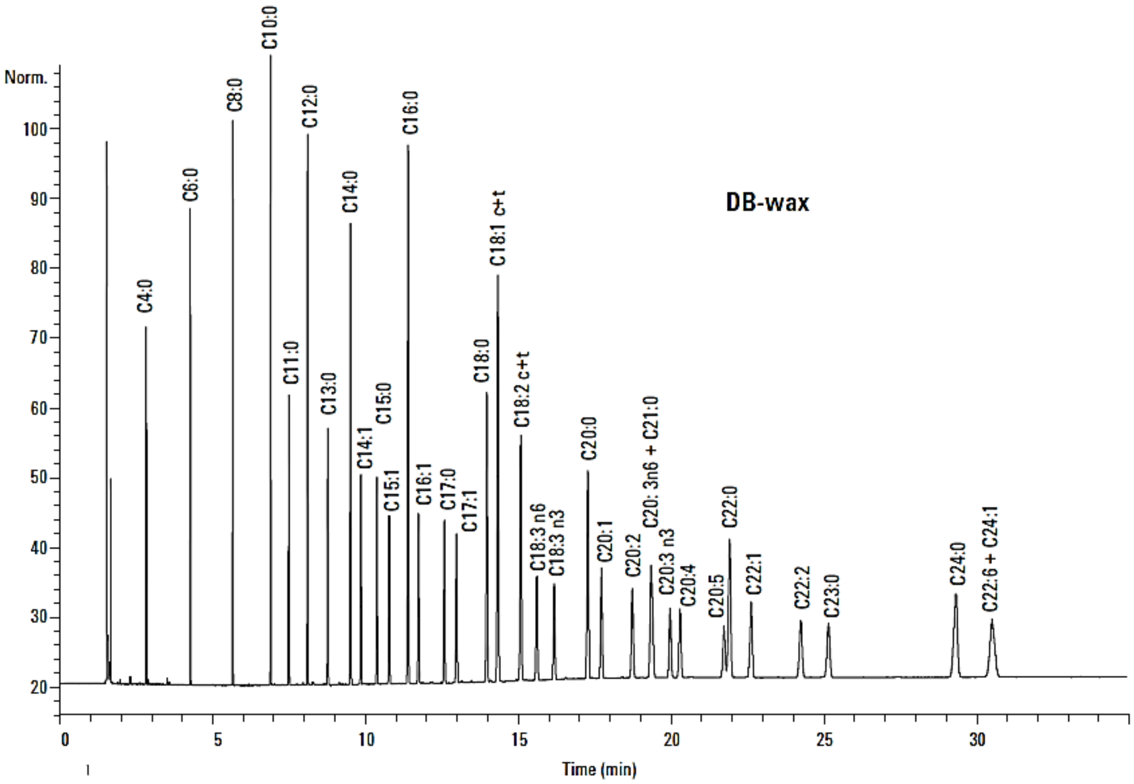


Figure 11. Chromatogram for de 37 component FAME mix from DB wax column. Source: Supelco (2005), [52].

The 37 FAME compounds mix analysis obtained using the Shimadzu equipment is presented in Figure 12.

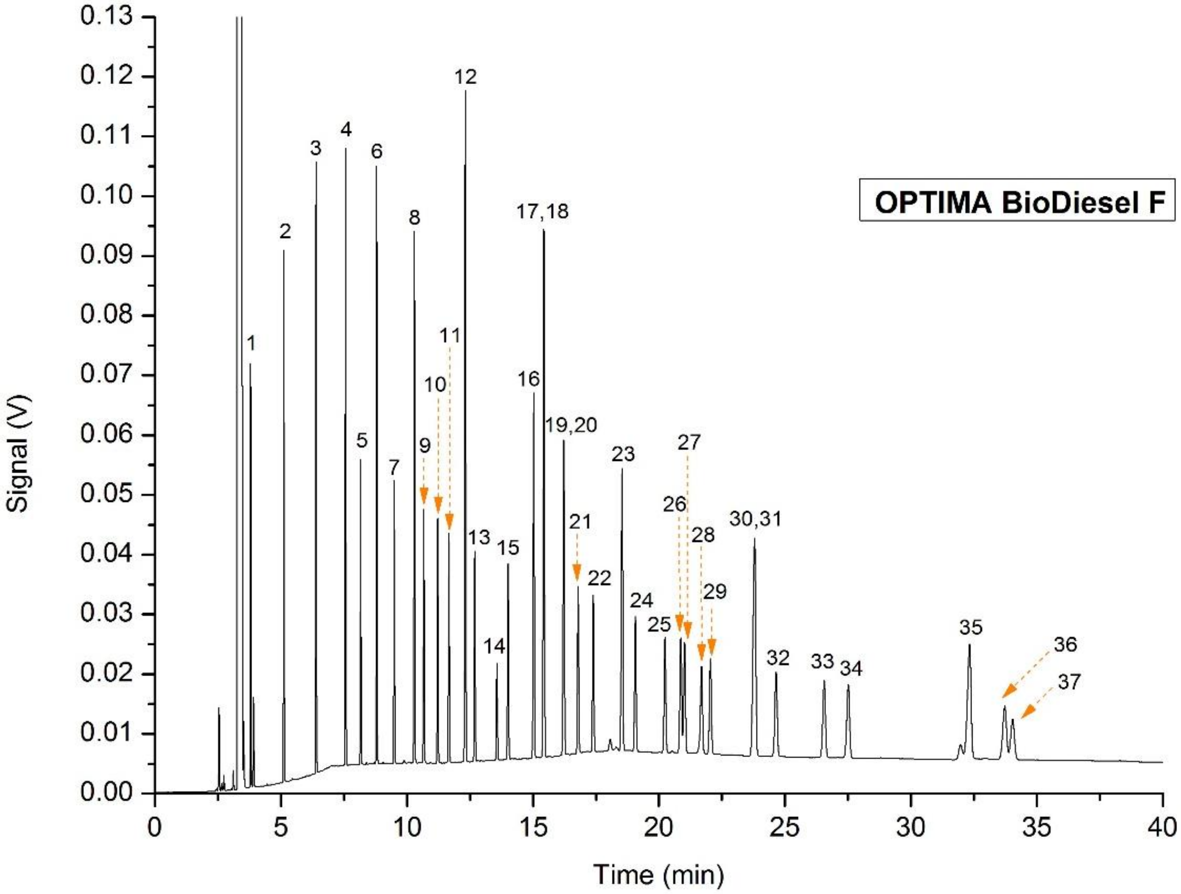


Figure 12. Chromatographic analysis obtained by GC-FID for the 37 compound FAME mix obtained using the Shimadzu using the Shimadzu equipment, using an OPTIMA BioDiesel F column.

Table 8 shows the peak number of each FAME, its name, the component identification number and the retention time. This table is used to identify the peaks, and quantify the FAMEs in the biodiesel samples.

Table 8. Elution order, compound name, Compound ID and retention time for 37 compound FAME mix.

Elution order	Compound name	Compound ID	Retention time (min)
1	Butyric acid methyl ester	C4:0	3.795
2	Caproic acid methyl ester	C6:0	5.113
3	Caprylic acid methyl ester	C8:0	6.392
4	Capric acid methyl ester	C10:0	7.563
5	Undecanoic acid methyl ester	C11:0	8.161
6	Lauric acid methyl ester	C12:0	8.796
7	Tridecanoic acid methyl ester	C13:0	9.492
8	Myristic acid methyl ester	C14:0	10.292
9	Myristoleic acd methyl ester	C14:1	10.667
10	Pentadecanoic acid methyl ester	C15:0	11.218
11	cis-10-Pentadecanoic acid methyl ester	C15:1	11.663
12	Palmitic acid methyl ester	C16:0	12.315
13	Palmitoleic acid methyl ester	C16:1	12.689
14	Heptadecanoic acid methyl ester	C17:0	13.569
15	cis-10-Heptadecanoic acid methyl ester	C17:1	14.011
16	Stearic acid methyl ester	C18:0	15.033
17,18	Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	14.432
19,20	Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	16.220
21	gamma-Linolenic acid methyl ester	C18:3n6	16.790
22	Linolenic acid methyl ester	C18:3n3	17.389
23	Arachidic acid methyl ester	C20:0	18.544
24	cis-11-Eicosenoic acid methyl ester	C20:1	19.070
25	cis-11,14-Eicosadienoic acid methyl ester	C20:2	20.245
26	cis-8,11,14-Eicosatrienoic acid methyl ester	C20:3n6	20.871
27	Heneicosanoic acid methyl ester	C21:0	21.021
28	cis-11,14,17-Eicosatrienoic acid methyl ester	C20:3n3	21.693
29	Arachidonic acid methyl ester	C20:4n6	22.049
30, 31	cis-5,8,11,14,17-Eicosapentaenoic acid methyl ester, Behenic acid methyl ester	C20:5n3 + C22:0	23.802
32	Erucic acid methyl ester	C22:1	24.651
33	cis-13,16-Docosadienoic acid methyl ester	C22:2	26.561
34	Tricosanoic acid methyl ester	C23:0	27.517
35	Lignoceric acid methyl ester	C24:0	32.331
36	cis-4,7,10,13,16,19-Docosahexanoic acid methyl ester	C22:6n3	33.726
37	Nervonic acid methyl ester	C24:1	34.035

After identification of all 37 compounds, the individual and the total chromatographic areas of FAMEs were used to quantify the FAME content present in biodiesel using the equation (5), according to EN14104 [49]:

$$C(\%) = \frac{(\sum A_{FAME} - A_{IS})}{A_{IS}} . \frac{m_{IS}}{m_{biodiesel}} \tag{5}$$

Where $\sum A_{FAME}$ is the sum of the areas of all FAMES (from C4:0 to C22:0), A_{IS} is the area of the internal standard (heptadecanoate methyl ester), m_{IS} is the mass of the internal standard and $m_{biodiesel}$ is the mass of biodiesel sample.

Similarly, the contribution of each FAME compound to the total FAMEs content was calculated to identify the esters formed in the reaction following the equation:

$$C_n(\%) = \frac{A_{FAME(n)}}{A_{IS}} . \frac{m_{IS}}{m_{biodiesel}} \tag{6}$$

Where $C_n(\%)$, is the contribution, in percentage, of FAME n in the sample, expressed in mass fraction and $A_{FAME(n)}$ is the area of the compound n.For the FAME content, only the methyl esters that contributed to the total content higher than 1% were considered.

3.3.4.1 Preparation of Methyl heptadecanoate solution

In order to quantify the FAME content present in the samples the internal standard method was adopted. To prepare the internal standard solution, 500 mg of methyl heptadecanoate was measured and transferred to a volumetric flask of 50 mL, and filling the remain volume with n-heptane to reach a final concentration of 10 mg/mL.

3.3.4.2 Derivatization of fatty acids by BF_3

In order to measure the maximum theoretical conversion, the derivatization of the methyl esters of fatty acids by BF_3 was used to study the distribution of all the fatty acids present in the feedstock used in the production of biodiesel. The derivatization of these compounds was carried out, that is, the transformation of the triglycerides and fatty acids present in the sample into methyl esters followed by the quantification of these compounds by gas chromatography.

To a 20 mL volumetric flask, 25 mg of the biodiesel sample and 2.5 mL of KOH solution (0.5 mol/L) were added. Then, the flask was closed and submitted to a drying process in an oven at 90 °C for 10 min. After this time, it was removed from the oven and allowed to cool to room temperature, and 2 mL of BF_3 in methanol solution (10%, v/v) was added. The flask was again closed and placed in the oven at 90 °C for more 30 min, then was removed from the oven and allowed to cool to room temperature.

Latter, 3 mL of methyl heptadecanoate solution was added and the solution was agitated using a vortex apparatus. Saturated sodium chloride, NaCl, solution (2 mL) was added and the solution was again subjected to the same homogenization procedure. The sample was centrifuged for 5 min at 3000 rpm for total separation of the two phases.

After centrifugation, 2 mL of the upper phase was withdrawn and added to a 4 mL flask. Anhydrous sodium sulfate was added in sufficient quantity to remove all moisture present. Gas chromatography analysis was then performed for fatty acids characterization present in the sample and to measure the experimental maximum conversion.

3.3.5 Kinetic study

The procedure was similar to the reaction presented in section 3.3.1. Throughout the reaction and at predetermined times (0, 15, 30, 60, 90, 120, 180, 240, 300, 360, 420 and 480 min), 1 mL of sample was removed from the reaction vessel using a micropipette and stored in a 2 mL vial. Immediately after cooling, the acidity decrease was measured to determine the conversion as indicated in section 3.3.3. The kinetic study was performed for different methanol:oil molar ratios (1:6; 1:8; 1:12; 1:15; 1:20; 1:25; 1:30 and 1:40), using a catalyst load of 10 %wt, 20% incorporation of OA acid and a reaction temperature of 65 ºC.

In a second experimental step, the determination of the activation energy for the reaction was conducted for different temperatures (50; 55; 60 and 65 °C) using the most promising molar ratio of oil/MeOH.

3.3.6 Ionic liquid recovery

The recovery of the ionic liquid was studied by measuring the number of times that the catalyst could be re-used without a significant decrease in its catalytic activity.

Previously, several experiments were carried out with the aim of determining the best recovery procedure for the studied catalyst, [BMIM]HSO_4. For these experiments waste cooking oil was used as a source of triglycerides, with no incorporation of OA, a catalyst load of 10 %wt, a reaction temperature of 65 °C, a molar ratio between methanol and oil of 20:1 and a reaction time of 4 h. Each experiment was performed according to the generic procedure described in section 3.3.1.

After this procedure, the vials of the aqueous phase were then submitted to a drying process using an oven at 110 ºC for 5 h. The dried samples were washed with distillated water in different proportions (1:0, 1:1, 1:1.5 and 1:3 %wt) and the same drying procedure was repeated. At the end of this procedure all samples were analyzed by FT-IR (Fourier transform infrared spectroscopy) to measure the correlation with the pure sample of [BMIM]HSO_4 and the effectiveness of the procedure.

Different drying processes were tested, the first of them submitted the sample to 5 h of drying at 110 ºC, and in the second, the sample stayed 1 h at 110 ºC and later during 15 h at 60 ºC. After these different processes the samples were washed with water in the same proportion and dried. Finally, the samples were analyzed in FT-IR to quantify their correlation with a pure sample of [BMIM]HSO_4. At the end of the whole procedure, it was possible to select the best methodology for recovery of ionic liquid. The analyzed responses were percentage of recovered mass and correlation with the pure sample of IL.

After the development of the ionic liquid recovery procedure, the production of biodiesel catalyzed by [BMIM]HSO_4 was carried out with waste cooking oil as raw material. The experimental conditions consisted of 40 % incorporation of OA, an oil/MeOH molar ratio of 20 %, a reaction temperature of 65 ° C and reaction time of 4 h. Following the methodology explained above the ionic liquid was recovered and then submitted to new reactions of biodiesel production with the same referred experimental reaction conditions to access its catalytic capacity. For this determination, the responses analyzed were the conversion estimated by the decrease in acid and the increase in content of FAMEs.

3.3.7 FT-IR qualitative analysis

The spectra were emitted between the wavenumber of 400 to 4500 cm^{-1} in a resolution of 4 cm^{-1} and 4 cumulative scans.

Figure 13 shows the equipment used for performing the FT-IR analysis.

Figure 13. PerkinElmer FT-IR, model Spectrum Two, spectrometry equipment.

4. RESULTS AND DISCUSSION

4.1 Feedstock characterization

The waste cooking oil (WCO) and oleic acid 90% (OA) were characterized by determination of the acid value (AV) and identification of the fatty acid profile followed by verification of the composition, following the procedures described in sections 3.3.3 and 3.3.4, respectively.

The acid value (AV) for the two samples of raw material was determined in triplicate and the results obtained are presented in Table 9.

The initial acidity index found for the studied WCO sample was 4.78 mg_{KOH}/g_{oil}. For the OA sample, the acid value determined was 177.04 mg_{KOH}/g_{OA}. Since the acid value is used to determine the amount of free fatty acids present in the oil samples and OA is a mix of fatty acids (mainly oleic acid), the higher value found for the OA sample is consistent. Compared to WCO, OA has a higher acid value. Therefore the introduction of controlled amounts of OA in the WCO samples allows the simulation of a high acidic waste oil feedstock.

Table 9. Characterization of the feedstock used in the production of biodiesel.

Sample	m_{sample} (g)	V_{KOH} (mL)	$C_{0\ KOH}$ (mol/L)	AV (mg_{KOH}/g_{sample})	$AV_{average}$ (mg_{KOH}/g_{sample})
Oleic acid (AO)	0.5003	22.70	0.06994	177.57	177.04
	0.5213	23.50		176.44	
	0.5371	24.30		177.10	
Waste cooking oil (WCO)	0.5233	0.64	0.06932	4.77	4.78
	0.5051	0.64		4.92	
	0.5188	0.62		4.64	

Posteriorly, the fatty acid profile in both samples of the feedstock was identified through the derivatization of the Fatty Acid Methyl Esters (FAME) by BF_3, followed by gas chromatography analysis. This analysis was performed in duplicate. The fatty acid profile for the waste cooking oil is presented in Figure 14.

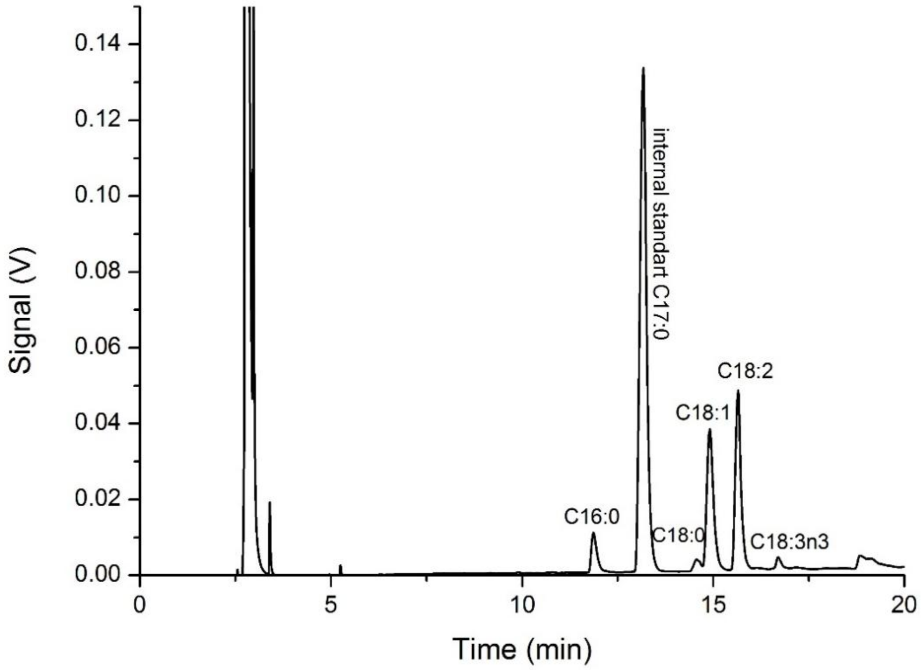


Figure 14. Chromatogram obtained after the derivatization of FAME from the waste cooking oil.

It can be observed that the main fatty acids constituting the analyzed WCO are: 10% of C16:0 (palmitic acid methyl ester), 1% of C18:0 (stearic acid methyl ester), 37.2% of C18:1 (oleic acid methyl ester), 43.4% of C18:2 (linoleic acid methyl ester), and 2.7% of C18:3n3 (linolenic acid methyl ester). Table 10 presents the qualitative and quantitative characterization of each fatty acid methyl ester in relation to two different samples of the waste cooking oil.

Table 10. Characterization of fatty acid methyl ester in waste cooking oil.

Peak name	**Peak ID**	**Sample 1**	**Sample 2**	**Average FAME (%)**
		FAME (%)	**FAME (%)**	
Myristoleic acd methyl ester	C14:1	1.8	0.1	1.0
Pentadecanoic acid methyl ester	C15:0	1.3	0.1	0.7
cis-10-Pentadecanoic acid methyl ester	C15:1	1.2	0.0	0.6
Palmitic acid methyl ester	C16:0	8.7	7.3	8.0
Stearic acid methyl ester	C18:0	2.7	2.5	2.6
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1 (c+t)	27.6	30.9	29.3
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2 (c+t)	32.8	35.6	34.2
gamma-Linolenic acid methyl ester	C18:3n6	0.4	0.2	0.3
Linolenic acid methyl ester	C18:3n3	2.0	2.2	2.1
Sum		**78.5**	**78.9**	**78.7**

According to Nurfitri *et al.* (2013) [8] and Ambat *et al.* (2018) [53], this composition profile is compatible with mixes containing sunflower oil, considering the greater content in linoleic acid (C18:2). Nurfitri *et al.* (2013) [8] presented a profile for sunflower oil with the following distribution in percentage: C16:0 (5.40), C16:1 (0.10), C18:0 (2.90), C18:1 (18.70), C18:2 (72.90) and C18:3 (-). Ambat *et al.* (2018) [53] determined the following profile: C16:0 (5-8), C18:0 (2-6), C18:1 (15-40), C18:2 (30-70) and C18:3 (3-5). Both distributions approximate the profile of methyl esters of fatty acids exhibited by this WCO sample.

Verma and Sharma (2016) [54] carried out a literature review, presenting the profile of FFA composition of different raw materials for the production of biodiesel. According to this review the typical composition profile of WCO is, inn percentage: C14:0 (0.19), C16:0 (4.1-26.5), C18:0 (1.4-10.9), C20:0 (0.55-2.30), C22:0 (0.65), C24:0 (0.04) C16:1 (0.80-2.4), C18:1 (38.6-44.7), C18:2 (32.8-36.0), C18:3 (0.2), C20: 1 (3.6), which is also close to the profile determined for the waste cooking oil used in this study.

Therefore, with this analysis it is possible to conclude that the raw material in question is similar to a waste sunflower oil.

On the other hand, the fatty acid profile of the OA sample is shown in Figure 15. It is concluded that in its composition other fatty acids besides oleic acid are present in smaller amounts.

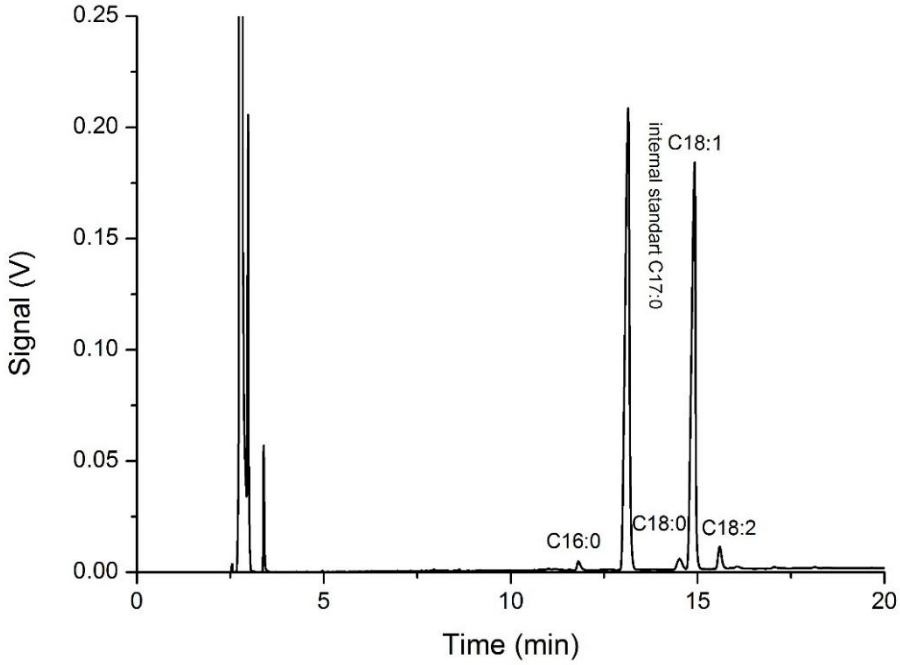


Figure 15. Chromatogram obtained after the derivatization of FAME from OA.

Table 11 describes the quantitative and qualitative profile of the fatty acids present in the analyzed sample of OA used as raw material in biodiesel production.

Table 11. Characterization of methyl ester fatty acid in OA.

Peak name	Peak ID	Sample 1	Sample 2	Average
		FAME (%)	FAME (%)	
Palmitic acid methyl ester	C16:0	1.6	1.8	1.7
Stearic acid methyl ester	C18:0	2.8	2.9	2.9
Oleic acid methyl ester, Elaidic acid methyl ester	C18:1(c+t)	87.2	87.3	87.3
Linoleic acid methyl ester, Linolelaidic acid methyl ester	C18:2(c+t)	4.6	4.5	4.5
Sum		**96.3**	**96.5**	**96.4**

With the analysis, it is possible to determine that the OA sample used consists of 87.3% C18:1 (oleic acid) and 10.7% (other fatty acids, 2% of which are unidentified). The determination of the oleic acid value contained in the sample was slightly less than the manufacturer's 90%wt reported reference value.

4.2 Experimental design

The optimization of the biodiesel production reaction was performed based on the Total Factorial Design 2^3, of three factors with two levels and in duplicate. From this method the combination matrix was determined with 16 runs. The parameters chosen as control factors were: A, percentage of OA incorporated in the WCO, B, oil/methanol molar ratio, and C, reaction time, with all factors adjusted at two levels (-1, +1). Two response variables were studied: R1, conversion of the simulated oil based on the reduction of acidity, and R2, content in FAME.

Table 12 describes the conditions applied in each run, both the design matrix and the actual values and their respective responses.

The evaluation of the responses was made separately. A different model was developed for each of the responses and different optimal conditions were estimated for the biodiesel production reaction. The conversion was determined by the variation between the initial acidity of the raw material (simulated oil) and the final acidity of the biodiesel produced, according to the procedure described in section 3.3.3. The FAME content was determined by gas chromatography analysis of the biodiesel produced, according to the procedure in section 3.3.4.

Table 12. Experimental design, real conditions and experimental responses of Experimental Design.

Run	Experimental Design			Real Conditions			Experimental Responses	
	Incorporation of OA (%wt)	Molar ratio oil/MeOH (mol/mol)	Reaction time (h)	Incorporation of OA (%wt)	Molar ratio oil/MeOH (mol/mol)	Reaction time (h)	Conversion (%)	FAME content (%wt)
	A	B	C	A	B	C		
1	1	1	1	40	1:40	8	79.3	30.1
2	-1	-1	-1	20	1:20	4	80.5	14.0
3	1	-1	1	40	1:20	8	82.6	36.9
4	-1	1	-1	20	1:40	4	84.6	18.0
5	-1	-1	1	20	1:20	8	88.4	23.9
6	1	1	1	40	1:40	8	80.0	32.8
7	1	-1	-1	40	1:20	4	75.4	32.3
8	-1	-1	1	20	1:20	8	87.2	22.8
9	-1	1	1	20	1:40	8	84.6	16.7
10	1	-1	-1	40	1:20	4	72.6	32.8
11	1	1	-1	40	1:40	4	78.5	33.0
12	1	1	-1	40	1:40	4	75.6	32.3
13	-1	1	-1	20	1:40	4	84.3	18.8
14	1	-1	1	40	1:20	8	80.0	37.7
15	-1	-1	-1	20	1:20	4	82.6	16.7
16	-1	1	1	20	1:40	8	87.4	18.9

4.2.1 Analysis for the conversion response (R1)

The analysis of variance (ANOVA), allows the comparison of the variation of the responses found for each combination of levels with the variation of the random errors associated to these responses. It takes into account the sources of imprecision and inaccuracy of the experiments. In this way it is possible to determine if the proposed regression is appropriate to the model [55].

Table 13 shows the ANOVA table for the conversion calculated from the reduction of acidity of the simulated oil whose value was calculated with the aid of the software Experimental Design 11.

Table 13. ANOVA table of conversion for α=0.05.

Source	Sum of Squares	df	Mean Square	Calculated F-value	Tabulated F- value	p-value	
Model	296.31	6	49.385	23.844	3.37	<0.0001	significant
A	193.21	1	193.210	93.288	5.12	<0.0001	
B	1.5625	1	1.562	0.754	5.12	0.408	
C	78.3225	1	78.322	37.816	5.12	0.0002	
AB	0.0225	1	0.0225	0.0108	5.12	0.919	
AC	1.1025	1	1.102	0.532	5.12	0.484	
BC	22.09	1	22.090	10.665	5.12	0.00975	
Residual	18.64	9	2.071				
Lack of Fit	0	1	0	0	238.9	1	not significant
Pure Error	18.64	8	2.330				
Cor Total	314.95	15					

The significance of the regression is evaluated by the Fisher test (F test), which consists of a comparison between $F_{calculated}$ and $F_{tabulated}$, which takes into account the degrees of freedom of both regression and residual. If the $F_{calculated}$ is larger than the $F_{tabulated}$, there is a significant difference between the treatments at the level of the error (α) applied. If the $F_{calculated}$ is smaller than the $F_{tabulated}$, it is concluded that there are no significant differences on the treatments. Another possibility is the comparison of the p-value with α. If the p-value is less than α, there is a significant difference between the treatments, if the p-value is higher than α, it is concluded that there are no significant differences on the treatments. The parameter α represents the level of significance of the statistical analysis. The lower the level of significance applied, the higher the level of confidence in the statistical test result.

According to the ANOVA for the conversion response (R1), the model is significant, because the value of $F_{calculated}$ equal to 28.844 is greater than the $F_{tabulated}$ of 3.370. The regression is statistically significant and, therefore, the model is well adjusted to the data, with a confidence level of 95% (α = 0.05). Another way to evaluate the model is to verify the lack of fit, the comparison between the $F_{tabulated}$ of 238.9 and the $F_{calculated}$ of 0 indicates the non-significance of the factor, because $F_{tabulated} > F_{calculated}$, that is, the errors of the model are due to random errors and to the system, and not to a problem with the adjustment of the data. Therefore, for this case, the model is significant, while the lack of adjustment is not.

For the analysis of variance of the conversion response, the significant factors are A (percentage of OA incorporation), C (reaction time) and the interactions AB and BC. The factor B (oil/methanol molar ratio) and the AB and AC interactions are not significant.

In this study, the p-value determines the order of significance of the factors, that is, the lower the p-value, the greater the influence of the factor on the results, thus, the decreasing order of significance of the factors is A (incorporation of OA), C (reaction time), BC interaction, B (oil/methanol molar ratio), AC interaction and AB interaction.

4.2.1.1 Residuals analyses for conversion

The quality of the adjustment was also assessed by the analysis of the determination coefficient, which was estimated as R^2= 0.9408 and the $R^2_{adjusted}$= 0.9014, indicating that the observed and predicted values are close and that the model can be used to predict responses. The proximity of these values indicates the non-occurrence of residues in the analysis since residues are the subtraction of the observed response of the expected response. The expectation is that the data are normally distributed within a straight diagonal line, with no residue occurring too far from the line. There are no outliers, that is, discrepant points that impair the adequacy of the model to the experimental data. Figure 16 shows the set of experimental data in question, normally distributed.

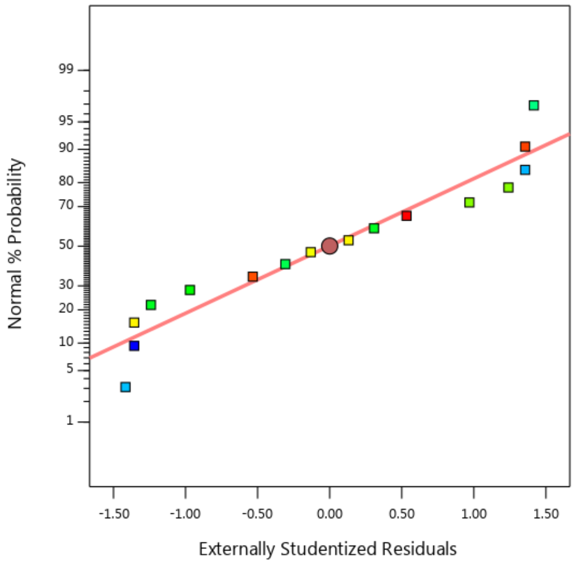


Figure 16. Normal plot of Residuals.

The residues versus predicted plotted in Figure 17 help to verify that the residues approach the null value and that the residues follow a specific standard. In this case the graph within the expected patterns, because the points are near the centerline. Another important aspect of this tool is to assist in the identification of outliers, which are runs which exhibit very large residues that should be discarded from the statistical evaluation.

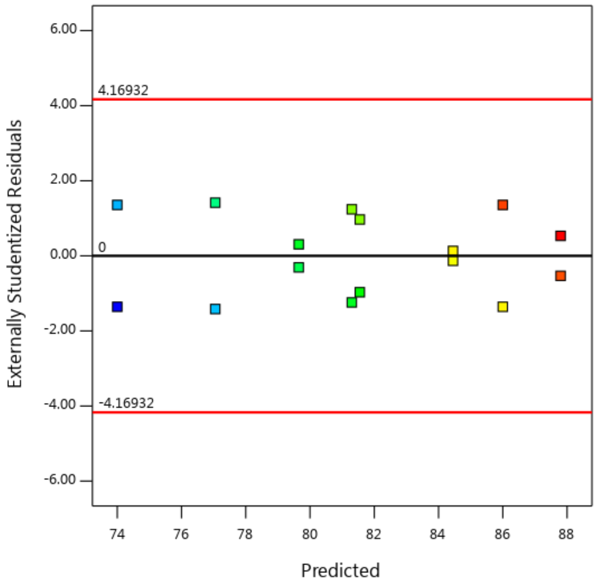


Figure 17. Residuals vs. Predicted.

Any value outside the red line in Figure 17 should be considered an outlier and the experiment or measurements of the responses should be repeated.

4.2.1.2 Effect of the factors on the conversion

The cube chart is a good analysis tool to predict the effects of factors and their levels, in which it presents the predicted mean values for each combination. Figure 18 illustrates, for all three factors, the adjusted means of the experimental conversion results for both levels, +1 and -1.

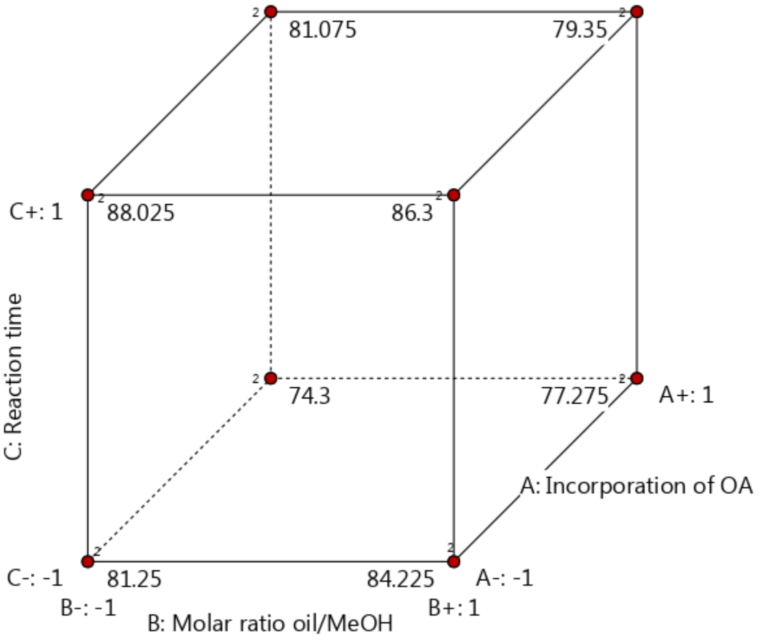
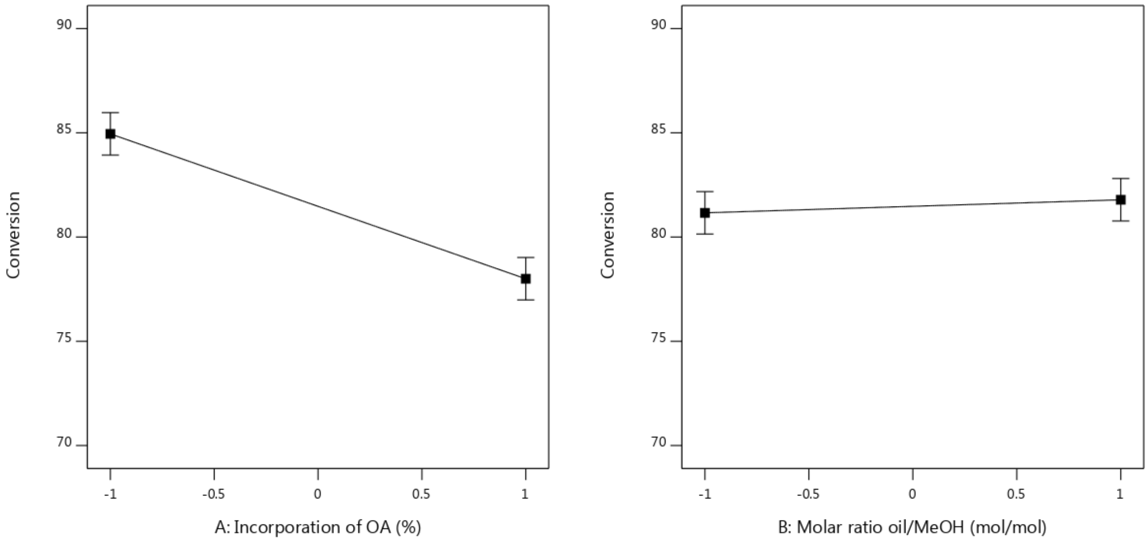


Figure 18. Cube chart for conversion.

The effects of the parameters are presented in Figure 19, where it can be seen the deviation of the adjusted means between the levels. When the factor has a positive effect, the conversion is expected to increase as this factor is changed to a higher value. The opposite also applies, when the factor has a negative effect the conversion increases as the factor is decreased in value.



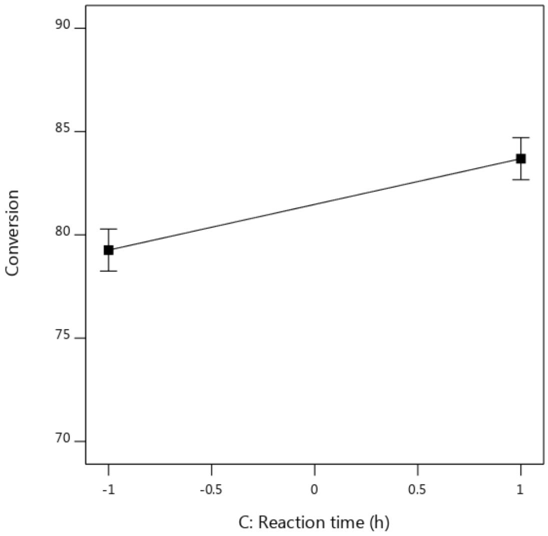


Figure 19. Effects for the conversion.

In this way it is possible to notice that the factor A has a negative effect due to the reduction in the conversion response, when the factor in the lower level is changed to the higher one, presenting a negative angular coefficient. On the other hand, factors B and C have a positive effect, because the response increases as it changes from the lowest to the highest level. Factor B does not have great influence on the response.

Parameters A and C have lines with slopes larger than parameter B, which means that they induce larger changes in the conversion values when changed.

Another important tool of statistical analysis is the response surface graph, which allows the interpretation of the influence of factors in pairs, showing the interaction between the variables, representing the response as a three-dimensional surface. The interpretation of this plot is done by checking the difference in the response between the levels of one factor and the levels of other factors. If this difference occurs in the responses, there is interaction between the factors.

The interaction plot illustrates the interaction of factor A levels with factor B levels. The establishment of parallel lines is interpreted as an indication that factor A and factor B do not interact with each other and that the effect of one factor does not depend on the other, that is, they are independent. The formation of non-parallel lines indicates that interaction occurs between the factors, that is, the factors besides influencing the result, also alter the effects of the other factors in the response.

Figure 20 shows the response surface relating to the influence of the variables: incorporation of OA (A) and molar ratio oil/methanol (B), and the interaction graph for these two variables.

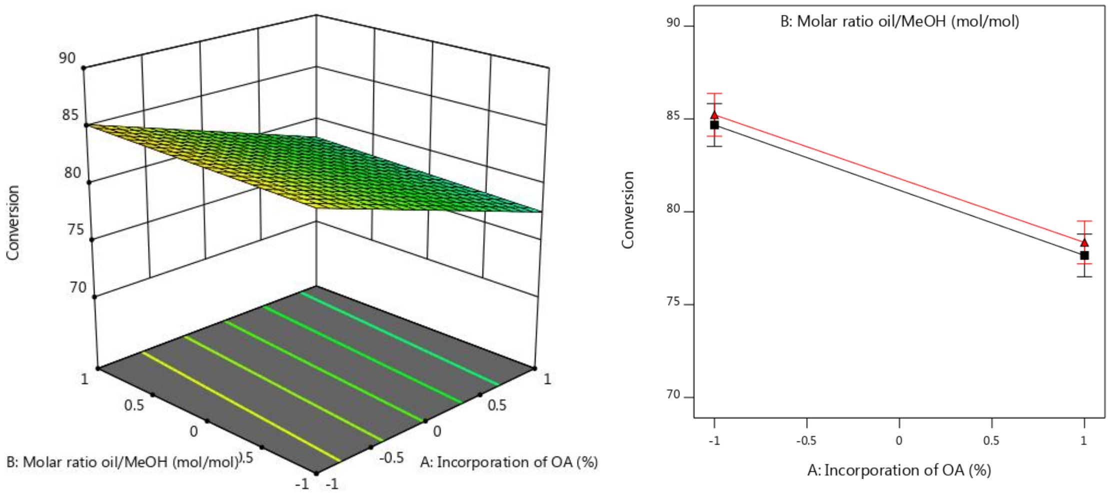


Figure 20. Response surface for the conversion being influenced by the incorporation of OA (A) and the molar ratio oil/MeOH (B) and interaction graph of these variables.

The response surface indicates that factor A has great influence on the conversion response, since observing the surface along axis A at a fixed point in B, a significant variation is verified.

It is observed a large differences in the slopes correspondent to the two factors. When the same analysis is done for factor B, it is clear that the conversion response hardly changes along the B axis between the levels. Then it is concluded that factor A has a greater influence on the conversion response than factor B.

In Figure 20, the lines that associate variables A and B are parallel lines that represent the lack of interaction between the factors for the studied response, that is, the effect caused by the change in the factor A level in the response is independent of the level of factor B and vice versa. The non-existence of this interaction is confirmed by the analysis of the p-value determined in ANOVA, where the AB interaction has no significance for the appropriate model.

Figure 21 shows the response surface with respect to the influence of the variables: incorporation of OA (A) and reaction time (C), and the interaction graph of these two variables.

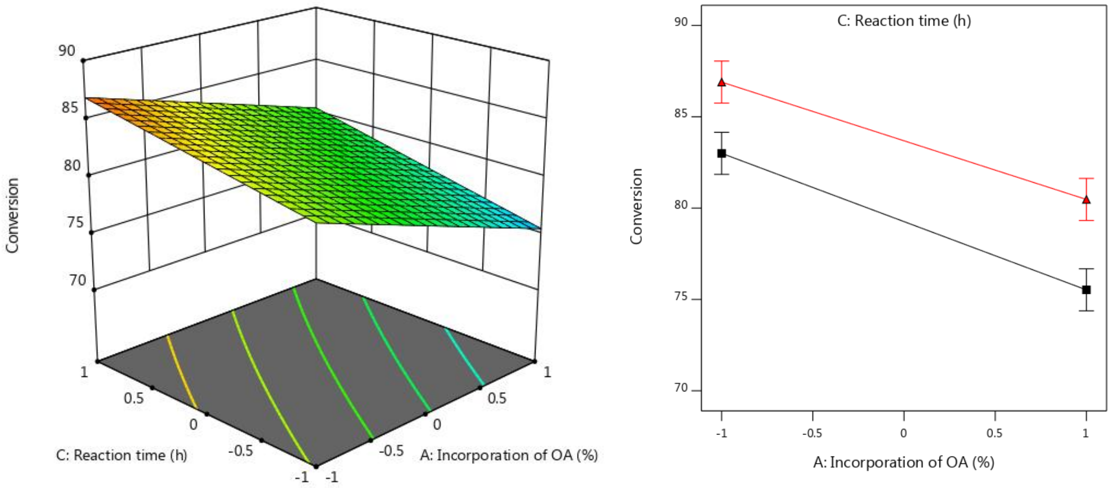


Figure 21. Response surface for the conversion being influenced by incorporation of OA (A) and the reaction time (C) and interaction graph of these variables.

The response surface indicates that variable A, as before, has a high influence on the conversion results. By observing the values along the axis A at a fixed point in C, we notice a significant variation in the slope between the levels of the factor. Analyzing now the slope variation in the lines concerning the C axis, a great variation between the values obtained between the studied levels is also observed. What is also evident is that factor A has a negative effect on the response and factor C has a positive effect, since the slopes of the lines between the levels for each of these factors show an opposite behavior, the first one decreases while the second one increases.

The interaction graph of factors A and C shows two parallel lines representing the lack of interaction between the factors to the studied response, that is, the effect caused by the change in the level of factor A in the response is independent of the level of factor C and vice versa. The non-existence of this interaction is confirmed by the analysis of the p-value determined in ANOVA, where the AC interaction has no significance for the appropriate model.

Figure 22 shows the response surface in relation to the influence of the variables: oil/methanol molar ratio (B) and reaction time (C) and the interaction graph of these two variables.

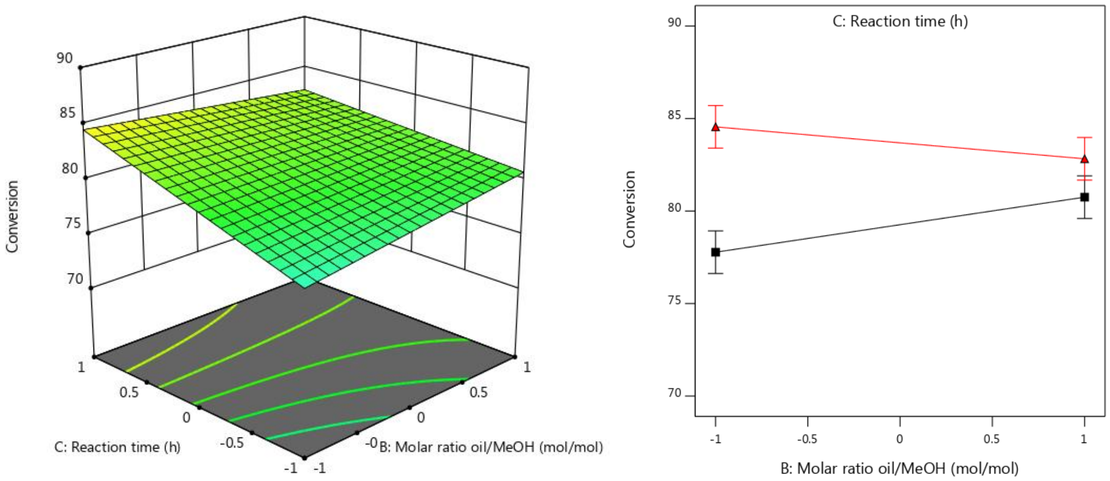


Figure 22. Response surface for the conversion being influenced by the molar ratio oil/MeOH (B) and reaction time (C) and the interaction graph of these variables.

The response surface indicates that variable B, as mentioned previously, has no influence on the conversion results since there is a practically null variation in the slope between the factor levels. However, by analyzing the slope variation in the line concerning the C axis, there is a considerable variation between the values obtained between the studied levels. Thus, factor C has a greater influence on the conversion response than factor B.

In the interaction graph between the variables, the non-parallel lines indicate the interaction between the factors. The effects of changing the B-level in response are dependent on factor C levels, and vice-versa. This fact confirms that among the three interactions of the factors, the interaction BC has greater significance as confirmed by the lower p-value determined in the ANOVA for the interactions, shown in Table 13.

4.2.1.3 Mathematical model for conversion (R1)

Table 14 shows the coefficients determined for the mathematical model constructed through the regression of the experimental data corresponding to the conversion response (R1). Using the calculated coefficients it is possible to construct the equation that best adapts to the total factorial studied. This model represents the way in which the factors studied and their interactions influence the conversion response. The model equation is represented by Equation (7).

Table 14. Coefficients for conversion model.

Coded factor	Coefficient
Independent	81.47
A	-3.48
B	0.3125
C	2.21
AB	0.0375
AC	0.2625
BC	-1.17

$$Y = 81.47 - 3.48A + 0.3125B + 2.21C + 0.0375AB + 0.2625AC - 1.17BC \quad (7)$$

In the equation it can be seen that Factor A and the interaction BC have a negative effect on the response, whereas factors B, C and other interactions have positive effects. The decreasing order of the influence of the factors was described as A>C>BC>B>AC>AB, and in the equation it is noted this characteristic by the respective multiplicative coefficients of each factor.

It can be noted that all the tools used for statistical interpretation, ANOVA table, response surface and mathematical model, lead to similar conclusions.

4.2.1.4 Best conditions estimation for conversion

For the studied conditions, factors and their respective levels, it was possible to determine the best conditions estimated for the attainment of the maximum conversion, using the simulated oil. The best conditions with coded and real values are presented in Table 15.

Table 15. Best conditions for conversion.

Factor	ID factor	Code	Real value
A	Incorporation of OA	-1	20%
B	Molar ratio oil/MeOH	-1	1:20 (mol/mol)
C	Reaction time	+1	8 h

Under these conditions we have an average conversion value of 87.8 and a FAME content of 23.0%wt for a confidence level of 95%.

Comparing the information presented in the literature review (see chapter 2) and summarized in Table 4, regarding reactions of biodiesel production catalyzed by the ionic liquid [BMIM]HSO_4, with the results shown in Table 15, it is seen that satisfactory values of conversion were obtained, especially when it is taken into account that in this work, waste cooking oil enriched with OA was used, in order to simulate high acidic waste oil feedstocks. Another fact is the non-use of secondary catalysts to increase the conversion. Table 4 presents the literature review on biodiesel production using [BMIM]HSO_4 as the catalyst and the respective conversions achieved.

Fauzi and Amin (2012) [32] identified the molar ratio of alcohol /oleic acid of 9:1, catalyst load of 3.4%wt, reaction time of 4 hours and the reaction temperature of 90 °C, as optimum conditions for the procedure biodiesel production by a esterification reaction. The authors concluded that the oleic acid conversion was 84.43% and that the variables that have the greatest influence in this process are the reaction temperature and the catalyst dosage.

Elsheikh et al. (2011) [35], conducting a study on the production of biodiesel from the transesterification reaction. They called the fuel like the article the matter and investigated some ionic liquids based on imidazolium, to ask what their catalytic potential. [BMIM]HSO_4 or less, having a conversion of 91.2% under optimum conditions: 4.4% by weight of catalyst concentration, moral ratio alcohol/oleic acid of 12:1, reaction temperature of 160 ° C and 120 min reaction.

Ullah et al. (2015) [3] conducted research on the production of biodiesel from a two-step process. In the first step, an esterification reaction was carried out from the waste cooking oil and methanol, catalyzed by [BMIM]HSO_4, with the best conditions for this step being a catalyst concentration of 5%wt, alcohol/oil molar ratio of 15:1, a reaction time of 60 min and the reaction temperature of 160 ºC. In the second step, KOH was used as the catalyst for the transesterification reaction, which was carried out at 60 ºC, with 1%wt of catalyst and reaction time of 60 min. At the end of the two steps, the total yield was 95.65%.

4.2.2 Analysis for FAME content response (R2)

The ANOVA table for the FAME content response (R2) was constructed in the same way than the one presented above for conversion response (R1), and it is shown in Table 16.

Table 16. ANOVA for FAME content for α=0.05.

Source	Sum of Squares	df	Mean Square	Calculated F-value	Tabulated F- value	p-value	
Model	977.99	6	163.00	112.15	3.37	<0.0001	significant
A	871.73	1	871.73	599.78	5.12	<0.0001	
B	17.02	1	17.02	11.71	5.12	0.0677	
C	29.98	1	29.98	20.62	5.12	0.0336	
AB	2.64	1	2.64	1.82	5.12	0.5208	
AC	3.71	1	3.71	2.55	5.12	0.4381	
BC	52.93	1	52.93	36.41	5.12	0.0255	
Residual	13.08	9	1.45				
Lack of Fit	1.76	1	1.76	1.24	238.9	0.2978	not significant
Pure Error	11.32	8	1.42				
Cor Total	991.07	15					

From the ANOVA, it is possible to note the significance of the model obtained for the FAME content response, when it compares the $F_{calculated}$ that has a value of 112.15 and the $F_{tabulated}$ that equals 3.37. So, $F_{calculated} > F_{tabulated}$ denoting the adequacy of the model. The comparison of the p-value of the model of <0.0001 with the assigned alpha 0.05, reaffirms the significance of the model, since $p<\alpha$ value. Thus, the regression is statistically significant and, therefore, the model fits well with the experimental data, with a confidence level of 95%.

In relation to the lack of fit, the comparison between $F_{tabulated}$, which shows a value of 238.9, with a $F_{calculated}$ of 1.24, indicates its non-significance since $F_{tabulated}>F_{calculated}$, that is, the errors of the model are due to random and inherent system errors, and do not relate to problems with the adjustment of the data. This conclusion reaffirms that for FAME content response, the model is significant, while the lack of fit is not.

For the analysis of variance of the FAME content response, the significant factors are A (percentage of OA incorporation), B (oil/methanol molar ratio), C (reaction time) and BC interaction, thus interactions AB and AC are not significant.

4.2.2.1 Residuals analyses for FAME content

The analysis of the residues is presented in the normal probability plot in Figure 23. The FAME content response data are normally distributed, spreaded very close to the diagonal line, indicating that the constructed model is reliable and significant. The determination coefficient was estimated as R^2= 0.9808 and the $R^2_{adjusted}$= 0.9680, which reinforces the fact that there is a good regression.

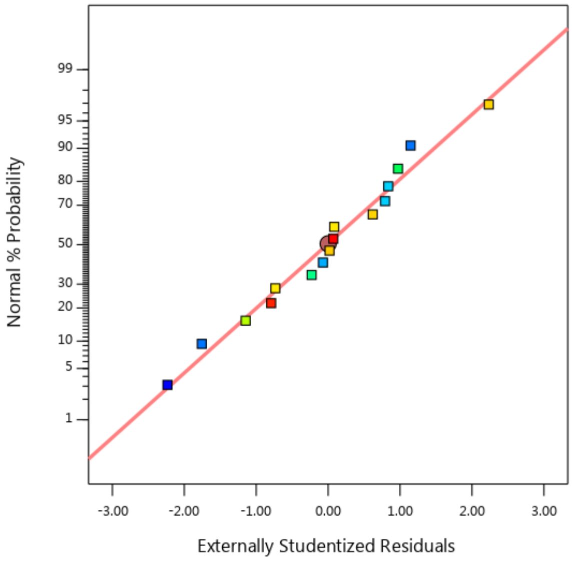


Figure 23. Normal plot of Residuals.

Figure 24 shows the graph of Residues vs. Predicted Values and allows to verify that the residues are independent of the level of the known variables and are distributed close to line 0, within the red lines, not showing outliers. These data reveal the good statistical quality of the data and the adequacy of the estimated mathematical model.

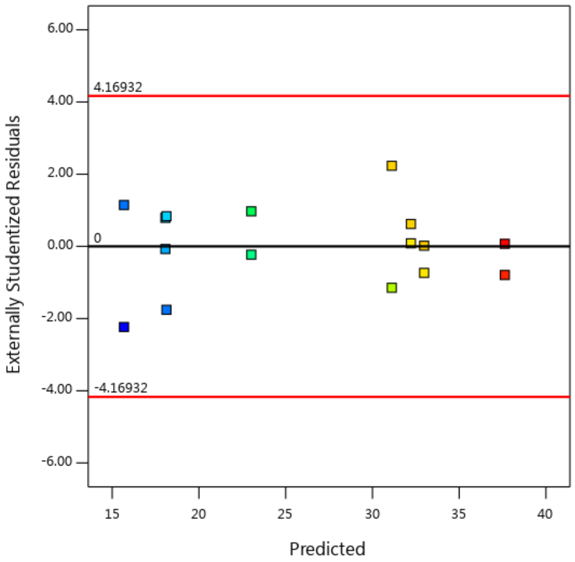


Figure 24. Residuals vs. Predicted.

4.2.2.2 *Effect of the factors on the FAME content*

Figure 25 shows the cube plot with the adjusted means for each combination of factor levels related to the FAME content response for the respective low and high levels of (A) incorporation of OA, (B) molar ratio of oil/methanol and (C) reaction time.

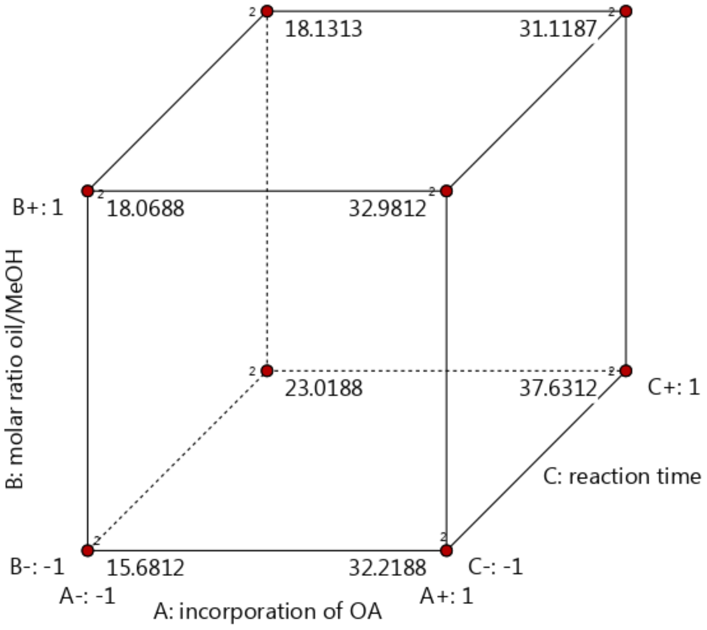


Figure 25. Cube chart for FAME.

The main effects of each parameter for FAME content are shown in Figure 26.

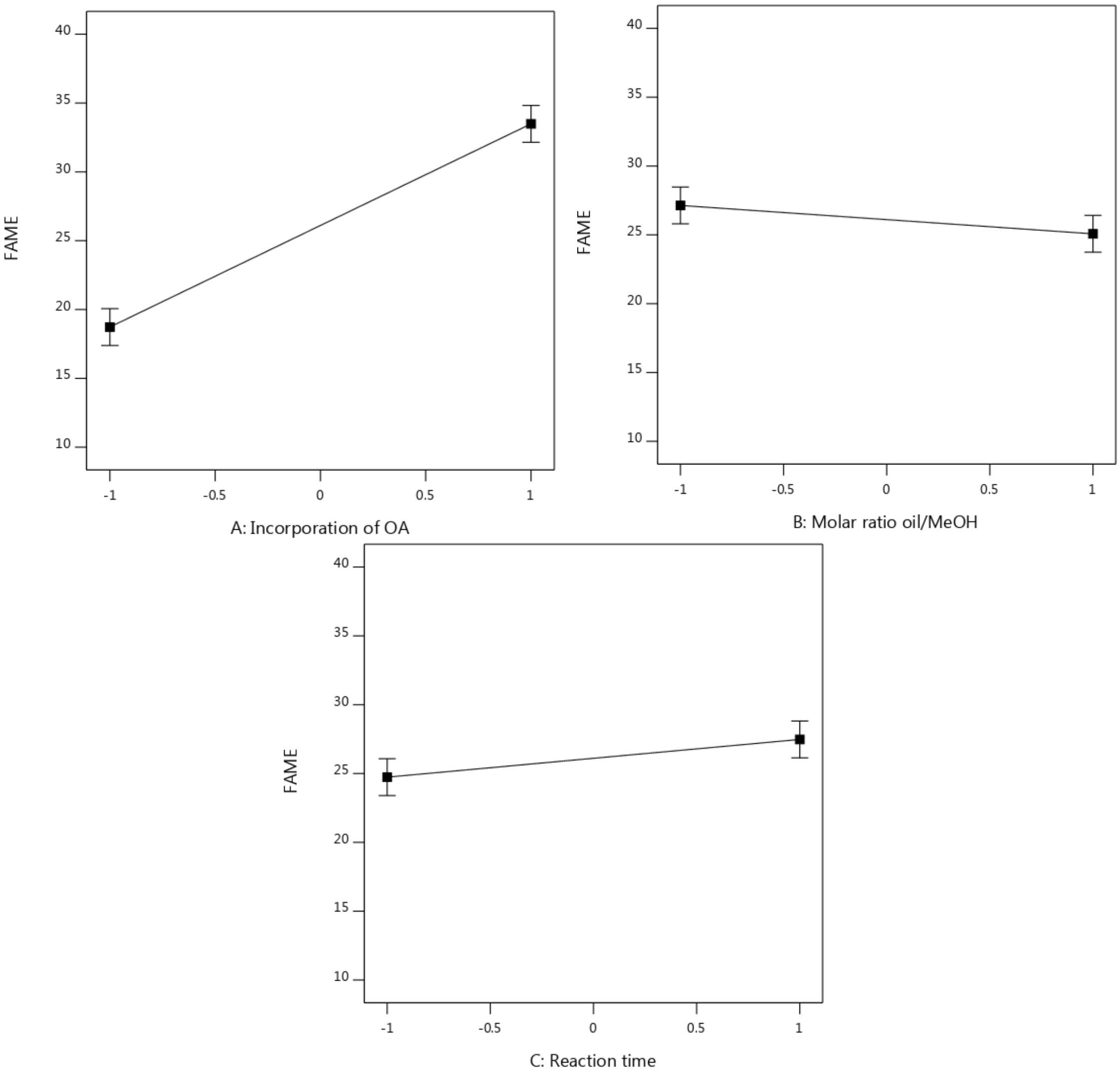


Figure 26. Effects for the FAME content.

The three parameters were significant, the main ones being those with more pronounced curves and expressing greater changes in the FAME content response values when levels change occurs. This is the case of factors A and C, both with a positive effect on the response. On the other hand, factor B shows a line with a low negative slope, which reveals that this effect has a negative effect on the FAME content response.

Figure 27 shows the response surface with respect to the influence of the variables: incorporation of OA (A) and molar ratio oil/methanol (B), and the interaction plot for these two variables.

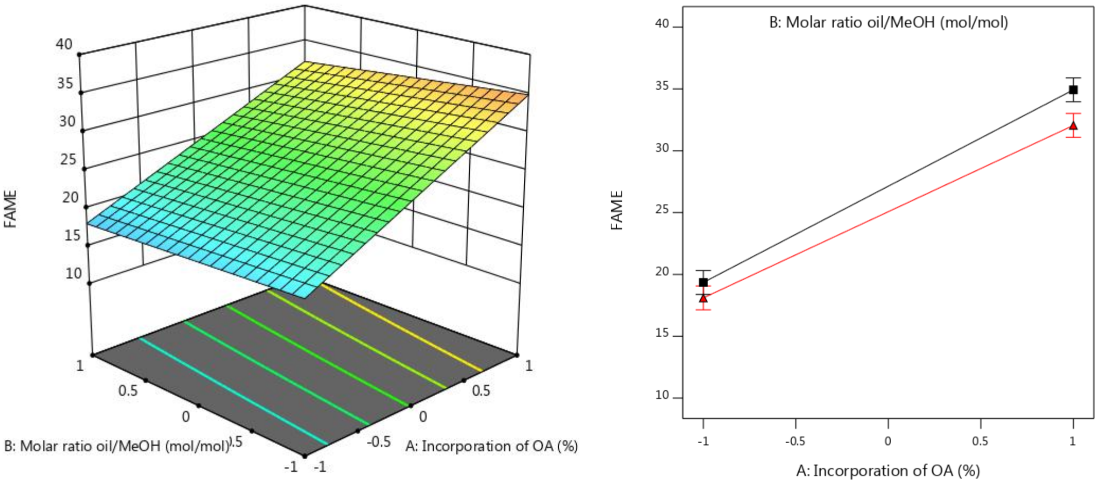


Figure 27. Response surface for the FAME content being influenced by incorporation of OA (A) and the molar ratio oil/MeOH (B) and interaction graph of these variables.

Doing the analysis in a similar way as the one presented above for the conversion response, it is possible to see that the response surface indicates that variable B has a low influence on the results of the FAME content, since there is only a small variation between factor levels. On the other hand, for variable A it is possible to verify that the response increases significantly when factor levels vary. Thus, factor A has greater influence on the FAME content response than factor B, and factor A shows a positive effect on the response.

The interaction plot of factors A and B shows two lines practically parallel which represent the absence of interaction between the factors in the response, that is, the effect caused by the change in the factor A level in the response is independent of the factor level B and vice versa. It is confirmed the non-existence of this interaction by the analysis of the p-value determined in ANOVA, where the interaction AB has no significance for the model developed.

Figure 28 shows the response surface in relation to the influence of the variables: incorporation of OA (A) and reaction time (C), and the interaction plot for these two variables.

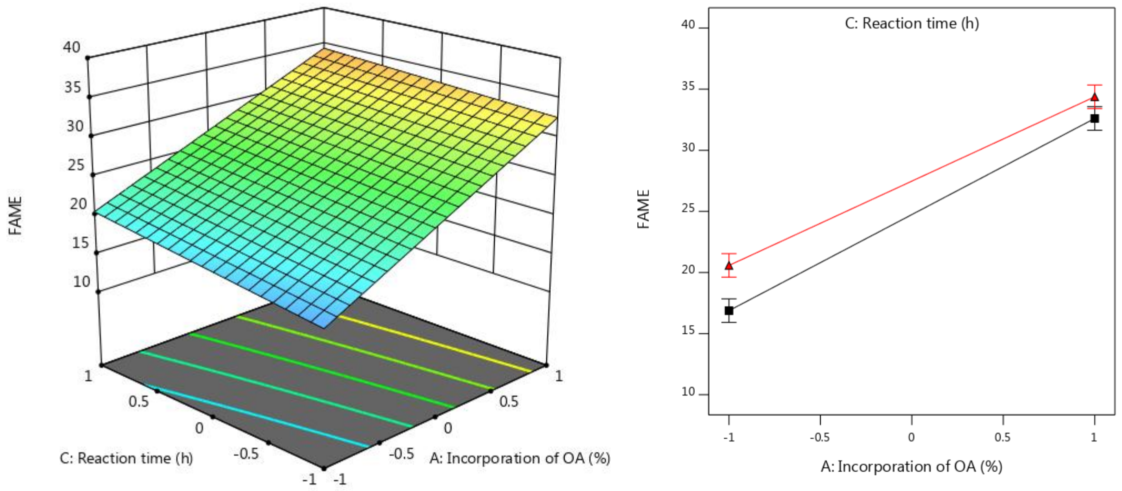


Figure 28. Response surface for the FAME content being influenced by incorporation of OA (A) and the reaction time (C) and interaction graph of these variables.

The response surface indicates that variable A, as already mentioned, has a high influence on the results. Thus, factor A has greater effect on the FAME content response than factor C, but factor C also shows influence on the system. Factors A and C exhibit a positive effect on the response.

The graph of interaction of factors A and C shows two practically parallel lines that represent the non-existence of interaction between the factors, that is, the effect caused in the change in the factor A level in the response is independent on the factor level C and vice versa.

Figure 29 shows the response surface with respect to the influence of the variables: oil/methanol molar ratio (B) and reaction time (C), and the interaction plot for these two variables.

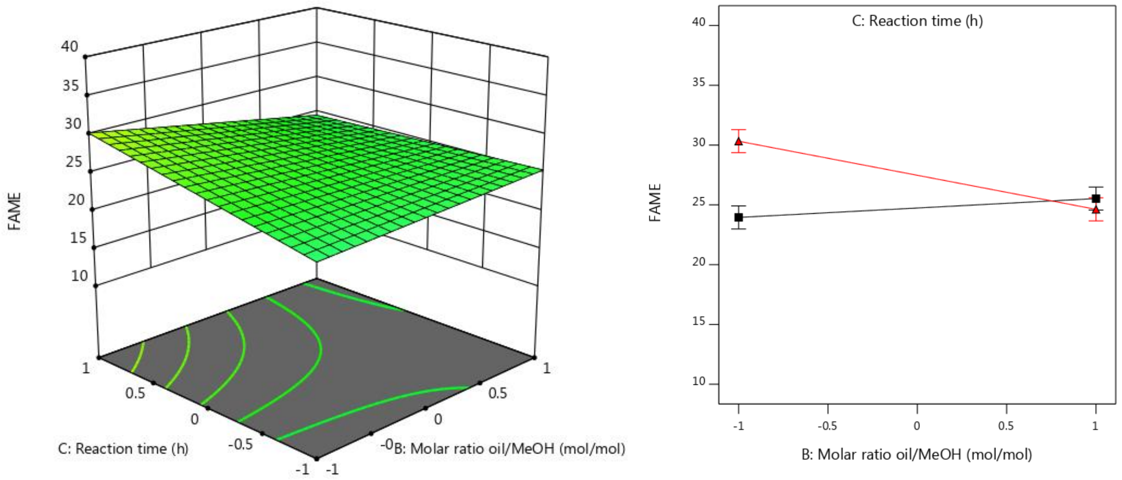


Figure 29. Response surface for the FAME content being influenced by molar ratio oil/MeOH (B) and reaction time (C) and interaction graph of these variables.

The response surface indicates that the variables B and C have low response variation when changing from the lowest to the highest level, but factor C shows a greater influence than factor B in the FAME content response.

The interaction plot of factors B and C shows two non-parallel lines that represent the presence of interaction between the factors for the result obtained, that is, the effect caused by the change in factor B level in the response is dependent on the factor level C and vice versa. The existence of this interaction is confirmed by the analysis of the p-value determined in ANOVA, where the BC interaction has significance for the appropriate model.

4.2.2.3 Mathematical model for FAME content (R2)

The multiple linear regression of the observed data led to the coefficients shown in Table 17. Equation (8) represents the way in which the factors studied and their interactions influence the studied response, showing the form of the model, relating to coded factors.

Table 17. Coefficients for FAME content model.

Coded factor	Coefficient
Independent	26.53
A	6.96
B	-1.09
C	1.31
AB	-0.3500
AC	-0.4250
BC	-1.40

$$Y = 26.53 + 6.96A - 1.09B + 1.31C - 0.3500AB - 0.4250AC - 1.40BC \qquad (8)$$

In equation (8) it can be seen that factors A and C have a positive effect on the response, while factor B and the three interactions studied have a negative effect. The decreasing order of factor influence and the interactions was described as A>BC>C>B>AC>AB, and in the equation this characteristic is confirmed by the coefficient values associated with each factor.

Again when comparing the three methodologies used to interpret the statistical responses they confirm and reinforce the conclusions.

4.2.2.4 *Best conditions estimation for FAME content*

For the studied conditions, factors and their respective levels, it was possible to determine the best conditions to obtain the maximum FAME content from the simulated oil. The best conditions with coded and real values are presented in Table 18.

Table 18. Best conditions for FAME content.

Factor	ID factor	Code	Real value
A	Incorporation of OA	+1	40%
B	Molar ratio oil/MeOH	-1	1:20 (mol/mol)
C	Reaction time	+1	8 h

Under these conditions an average value of FAME content of 37.6%wt and conversion of 81.3% are obtained, for a confidence level of 95%.

In order to maximize both responses the best conditions are explained in Table 19.

Table 19. Best conditions for both responses.

Factor	ID factor	Code	Real value
A	Incorporation of OA	+0.7298	37.3%
B	Molar ratio oil/MeOH	-1	1:20 (mol/mol)
C	Reaction time	+1	8 h

Under these conditions there is an average FAME content value of 35.6%wt and conversion of 82.2% to a confidence level of 95%.

When comparing these results with the literature review presented in chapter 2, it can be seen that satisfactory values of FAME content were obtained.

From all of the results discussed above, it was possible to conclude that the esterification reaction occurred in a much larger proportion than the transesterification reaction. This fact is supported by the fact that the content of FAME produced, in most cases, is less than the percentage of OA incorporated in the simulated oil, and the FAME produced are essentially composed of methyl esters of oleic acid.

4.3 Kinetic studies

For the kinetic study, only the esterification reaction was considered, since it can be concluded that in the studied conditions the transesterification reaction does not occur at a significant extent.

The reaction of esterification of oleic acid with methanol is an equilibrium reaction that can be represented by equation (9). The reaction rate can be described by equation (10), where OA stands for oleic acid, MeOH stands for methanol, PB means produced biodiesel, *a*, *b* and *c* are their respective reaction orders, and *d* is the reaction order related to water. The reaction rate constant for the direct reaction is k_1 while k_{-1} is the reaction rate constant for the inverse reaction.

$$C_{18}H_{34}O_2 + CH_3OH \rightleftharpoons C_{19}H_{36}O_2 + H_2O \tag{9}$$

$$-r_{OA} = k_1 C_{OA}^{a} . C_{MeOH}^{b} - k_{-1} C_{PB}^{c} . C_{H_2O}^{d} \tag{10}$$

Knowing that methanol is used in a large excess in the reaction tests, it can be assumed that the equilibrium is displaced to the formation of products, and it can also be admitted that the concentration of methanol is practically constant during the whole reaction. Therefore the rate of the direct reaction is much greater than the rate of the inverse reaction at the beginning of the reaction. Taking into account these assumptions, the Equation (10) can be simplified to Equation (11), where only the concentration of oleic acid is relevant for the reaction rate.

$$-r_{OA} = \frac{dC_{OA}}{dt} = k' C_{OA}^{a} \tag{11}$$

In order to determine the order of reaction and to study the behavior of the esterification reaction with an alcohol quantity increment, a set of experiments was performed in the same way as before, simulating a high acidity oil, incorporating a proportion of OA, defined herein as being 20%wt. In addition to this parameter, other operational conditions were also fixed: reaction time was set at 8 h and catalyst load at 10%wt. In the first part of this study the reaction temperature was kept constant at 65 °C and the molar ratio of oil/MeOH varied (1:6, 1:8, 1:12, 1:15, 1:20, 1:25, 1:30 and 1:40).

As only the esterification reaction, that is, the conversion of carboxylic acid to ester occurred, the initial concentration of the reactant calculation was carried out, considering that all the free fatty acids present in the waste cooking oil, determined by its acid value, were oleic acid, and then it was possible to calculate the estimated initial amount of oleic acid in the simulated oil samples. Then, having the initial concentration value for the acid and the conversion values estimated by the acidity drop in the reaction mixture at each predetermined reaction time, the acid concentrations could be calculated at those times.

A 1 mL of sample was withdrawn from the reaction mixture at predetermined times (0, 15, 30, 60, 90, 120, 180, 240, 300, 360, 420, 480 and 480 min). The acid value of each sample was determined following EN 14104 [49] and the conversion was estimated by comparing the initial and final values of the acid, according to equations (1) and (2) of section 3.3.3. The initial value of the acid was considered to be the acid value of the reaction mixture at 0 min.

Figure 30 shows the data obtained from each reaction for the acid value of the reaction mixture and conversion of oleic acid versus time.

With these data it is evident that by increasing the molar ratio of oil/alcohol added to the reaction, the acid value decreases and the conversion increases. For a reaction time of 8 h the conversion reaches a limit of 70% with a ratio of 1:25 oil/MeOH, repeating this result for the ratios of 1:30 and 1:40. Figures 31 and 32 exhibit this conclusion more clearly, with the curves plotted on the same graph.

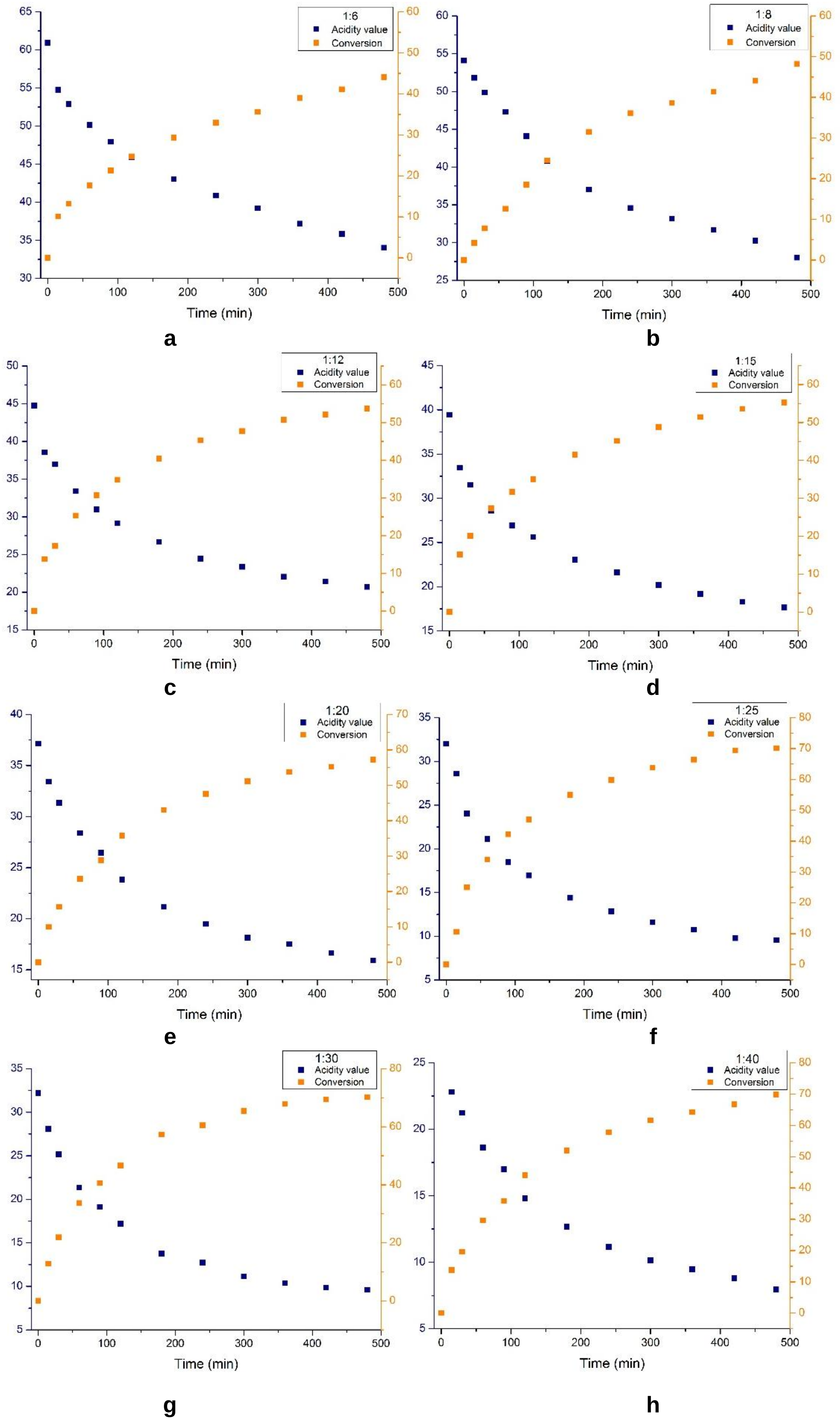


Figure 30. Acidity value (mg$_{KOH}$/g$_{sample}$) and conversion (%) versus time for different molar ratio oil/MeOH conditions.

a: 1:6; **b**: 1:8; **c**: 1:12; **d**: 1:15; **e**: 1:20; **f**: 1:25; **g**: 1:30; **h**: 1:40.

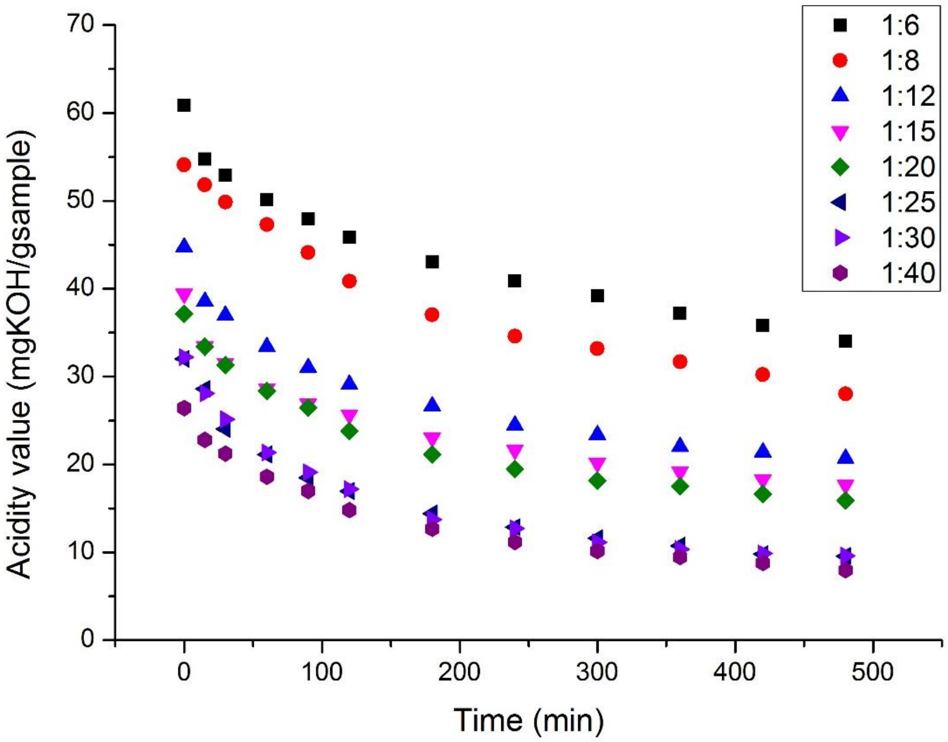


Figure 31. Reduction of acidity value for all conditions for different molar ratio oil/MeOH.

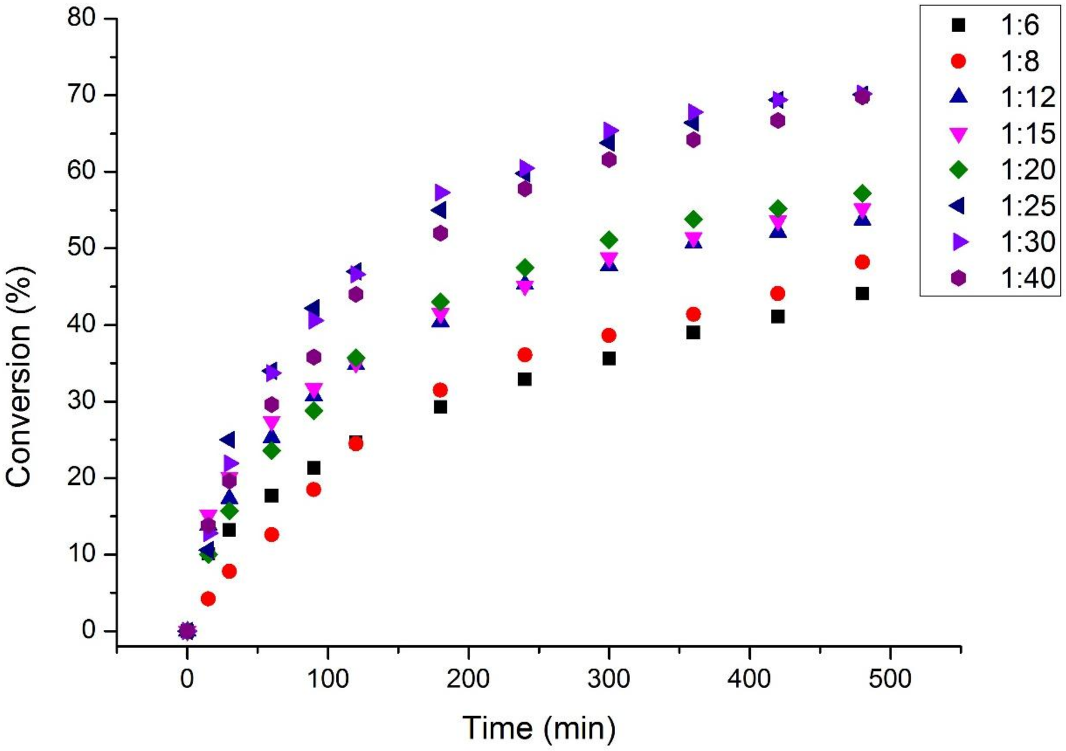


Figure 32. Conversion for all conditions for different molar ratio oil/MeOH.

In order to determine the order of reaction in relation to oleic acid, the Integral Method was used, applied to 0th, 1st, 2nd and 3rd order kinetic models, for all oil/methanol molar ratio tests implemented. Equation (11) was integrated with a α variating from 0 to 3, giving rise to equations (12) to (15).

0th order
$$C_{OA} = C_{OA_0} - k't \quad (12)$$

1st order
$$\ln C_{OA} = \ln C_{OA_0} - k't \quad (13)$$

2nd order
$$\frac{1}{C_{OA}} = \frac{1}{C_{OA_0}} + k't \quad (14)$$

3rd order
$$\frac{1}{C_{OA}^2} = \frac{1}{C_{OA_0}^2} + 2k't \quad (15)$$

The data were then plotted for each order of reaction, and the coefficient of determination (R^2) was used to determine the apparent order of the reaction. The coefficients of determination for each molar ratio and each test are given in Table 20.

Table 20. Coefficients of determination for each molar ratio oil/MeOH and each order.

Molar ratio oil/MeOH (mol/mol)	**R^2**			
	0th order	**1st order**	**2nd order**	**3rd order**
1:6	0.8964	0.9410	0.9724	0.9901
1:8	0.9198	0.9566	0.9817	0.9930
1:12	0.8289	0.8988	0.9504	0.9824
1:15	0.8278	0.9050	0.9592	0.9894
1:20	0.8519	0.9171	0.9639	0.9904
1:25	0.8011	0.9111	0.9780	0.9975
1:30	0.8264	0.9195	0.9773	0.9966
1:40	0.8500	0.9398	0.9895	0.9955

It is possible to note that the highest coefficient of determination in all cases is for the third order reactions, making it evident that the esterification reaction of oleic acid can be modeled as a 3rd order reaction.

Using Equation (15) (the integrated form of the reaction rate for a 3rd order equation), it is possible to estimate the value of k' for each molar ratio oil/MeOH. These values are shown in Table 21.

Table 21. Kinetic constants for each molar ratio oil/MeOH.

Molar ratio oil/MeOH (mol/mol)	k' ($L^2.mol^{-2}.min^{-1}$)
1:6	1,00E-04
1:8	1,50E-04
1:12	2,50E-04
1:15	2,50E-04
1:20	4,00E-04
1:25	1,10E-03
1:30	1,25E-03
1:40	1,60E-03

Assuming that the esterification reaction of oleic acid shows a third order kinetics, it was possible to estimate the activation energy of this reaction. For this reason, the molar ratio oil/MeOH of 1:30 was chosen, since a conversion of 70% in 8 h reaction was obtained in these conditions. The reaction tests were carried out with a temperature variation (45, 50, 55, 60, 65 °C), maintaining all the other operational conditions fixed and using the procedure described above.

In these tests, acidity reduction and conversion plots were also obtained (see Figures 33 and 34). It is easy to notice that with the increase in temperature the acidity values assume lower values while the conversion reaches higher values. For a reaction time of 8 h, a conversion of 51% was achieved at a temperature of 45 °C, while 55% conversion was reached for a temperature of 50 °C. At a temperature 55 °C it was obtained 60% conversion, and 66% conversion was attained for a temperature of 60 °C. Finally, a 70% conversion was reached for the temperature of 65 °C.

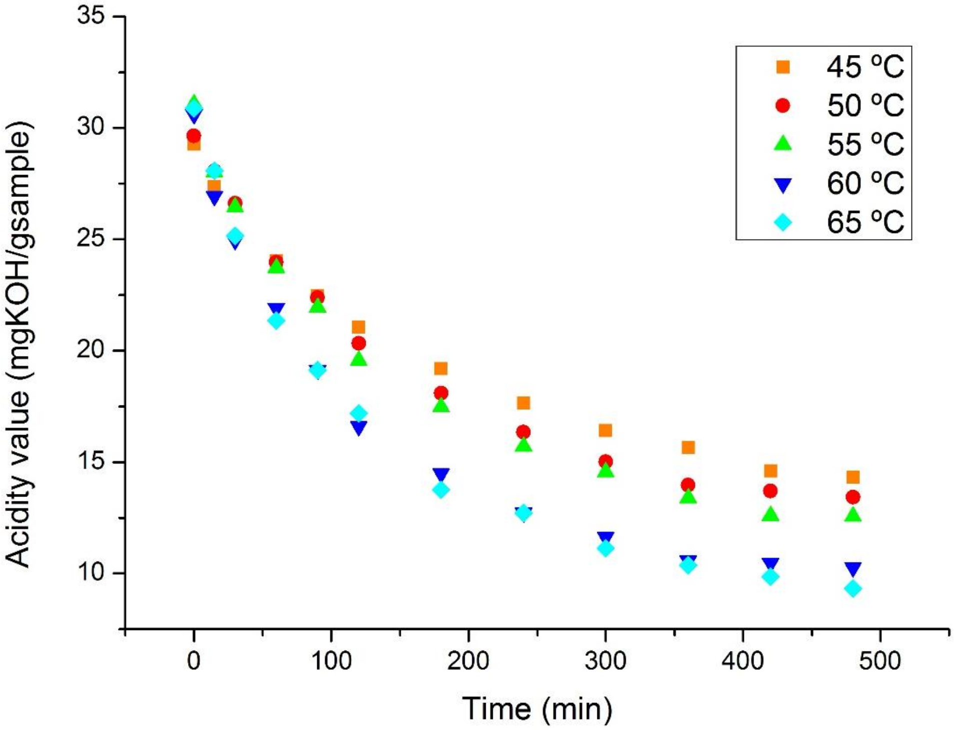


Figure 33. Reduction of acidity value for all temperature conditions.

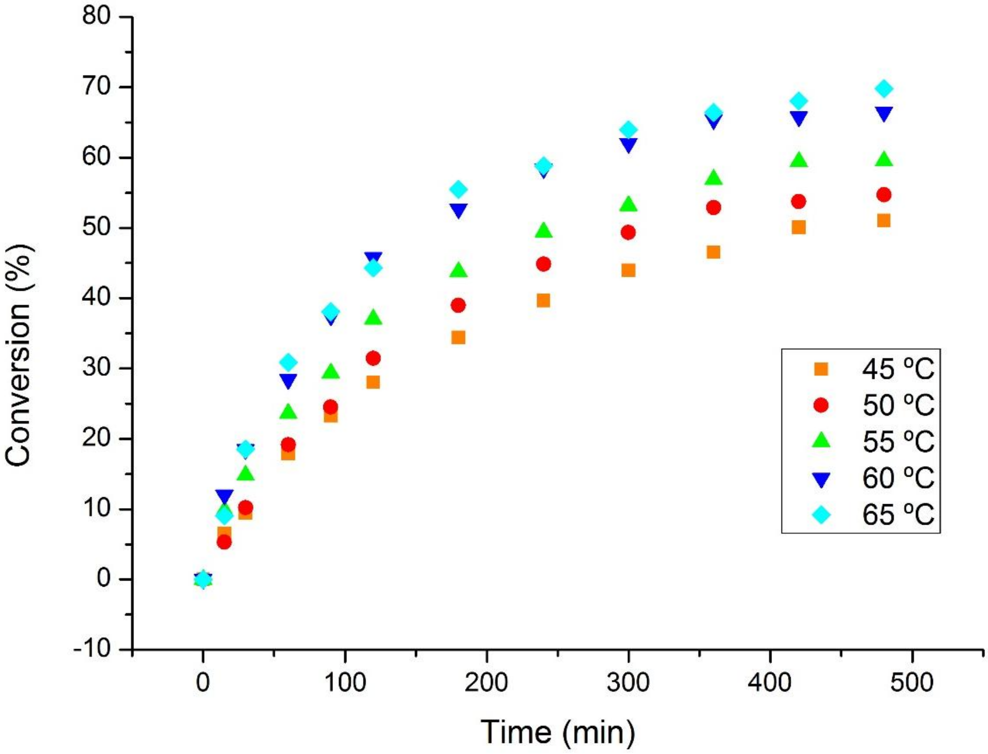


Figure 34. Conversion for all temperature conditions.

In the same way as previously proposed, the order of the esterification reaction was analyzed. Again, analyzing the determination coefficients, it is concluded that a third-order kinetics best fits the reaction data. The results of this study are shown in Table 22.

Table 22. Coefficients of determination for each temperature and each order.

Temperature (ºC)	**R²**			
	0th order	**1st order**	**2nd order**	**3rd order**
45	0.9037	0.9502	0.9814	0.9962
50	0.8837	0.9342	0.9686	0.9862
55	0.8677	0.9329	0.9747	0.9920
60	0,8162	0.9009	0.9568	0.9820
65	0.8264	0.9195	0.9773	0.9966

Using Equation (15) (the integrated form of the reaction rate for a 3rd order equation), it is possible to estimate the value of k' for each temperature. These values are shown in Table 23.

Table 23. Kinetic constants for each temperature.

Temperature (ºC)	***k'*** **($L^2.mol^{-2}.min^{-1}$)**
45	4,00E-04
50	5,50E-04
55	6,00E-04
60	1,05E-03
65	1,25E-03

The kinetic constant k' is related to temperature by the Arrhenius Equation which is given by Equation (16).

$$k' = k_0 exp^{\frac{-Ea}{RT}} \tag{16}$$

Where k' is the kinetic constant at a given temperature, k_0 is the pre-exponential factor, E_a is the activation energy, in kJ/mol, R is the gas constant, in kJ/(mol.K), and T is the temperature in K. When linearized, the Arrhenius equation takes the form of Equation (17):

$$lnk' = lnk_0 - \frac{Ea}{RT} \quad (17)$$

Therefore, by plotting the inverse of the temperature in K and the natural logarithm of the kinetic constant at each temperature, it is possible to estimate the activation energy for the reaction. The Arrhenius plot is shown in Figure 35.
A determination coefficient of $R^2 = 0.9536$ was obtained. The pre-exponential factor (k_0) was estimated at 2.46×10^3 $L^2.mol^{-2}s^{-1}$ and the activation energy (E_a) as 52.2 kJ/mol. This considerable activation energy indicates a dependence on temperature, being highly influenced by it.

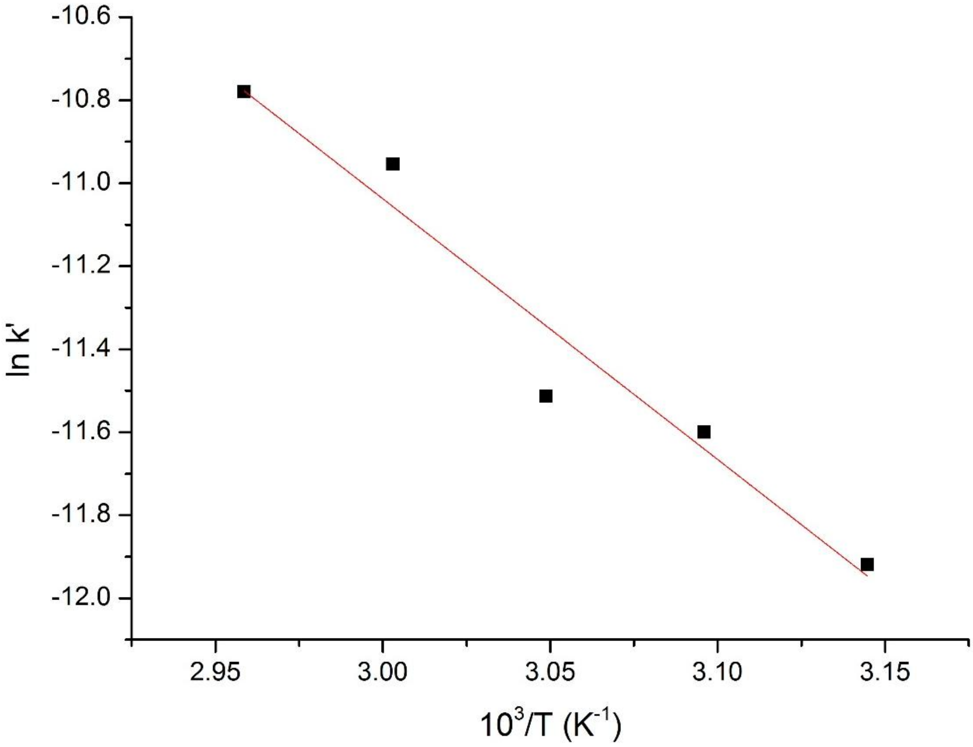


Figure 35. Arrhenius plot for the experimental data.

When the results are compared with the data presented the Table 5 in section 2.1.7, it can be concluded that the esterification reaction of the simulated acidic oil catalyzed with the ionic liquid [BMIM]HSO_4 has an activation energy close to other processes of biodiesel production already reported. One example is the study of the esterification reaction of palm oil catalyzed by H_2SO_4 at temperatures between 45 and 65 °C, which reaches 75.50 kJ/mol for the activation energy.

This process is followed by a KOH catalyzed transesterification reaction of the same oil at the same temperatures, where the values of 1.45, 328 and 89.35 kJ/mol are obtained for the conversion of the triglyceride to diglyceride, monoglyceride and glycerol, respectively. The research also revealed that the esterification reaction fits to a first order reaction, and the transesterification reaction is characterized by a second order reaction [41].

Another study that estimated the activation energy was the study of the transesterification of palm oil through microwave, catalyzed by [HSO_3-BMIM] HSO_4 at a temperature of 108 ºC. The study revealed an activation energy under these conditions of 56.12 kJ/mol, assuming a 1st order reaction [46].

Another research shows that the reaction of esterification of oleic acid with ethanol, catalyzed by $SnCl_2.2H_2O$, at temperatures between 45 and 75 ºC exhibits an activation energy of 46.69 kJ/mol and it is characterized as a first order reaction [40].

4.4 Recovery of ionic liquid

4.4.1 Alternatives for [BMIM]HSO_4 IL recovery

Tests for IL recovery were performed using waste cooking oils as a source of triglycerides, without incorporating OA, for catalyst loads of 10%wt, reaction temperature at 65 °C, molar ratio of methanol to oil of 20:1, and reaction times of 4 h.

The biodiesel production was carried out according to the procedure described in section 3.3.1. After the reaction, the flasks of the aqueous phase were then subjected to a drying process for 5 h in an oven at 110 °C. Subsequently, the dried samples were washed with water in different weight ratios (1:0, 1:1, 1:1.5 and 1:3 sample/water) and again the same drying procedure was applied. At the end of the procedure all samples were analyzed by FT-IR to determine the correlation with a non-used sample of [BMIM]HSO_4 for an assessment of the effectiveness of the recovery procedure. The results obtained are presented in Table 24.

Table 24. Results of different proportions of washes with water.

Washing	Mass recoverd (%)	Correlation (%)
Without washing	110	88.9
1:1	91	95.5
1:1.5	94	95.8
1:3	97	97.8

From the data shown in the table above, it can be seen that the procedure which provides a higher recovery yield of IL, with a higher level of purity, is the one in which more water is used, 1:3 sample/water. Figure 36 shows the spectra of the different recovered IL samples using the distinct washing procedures, obtained by FT-IR analysis.

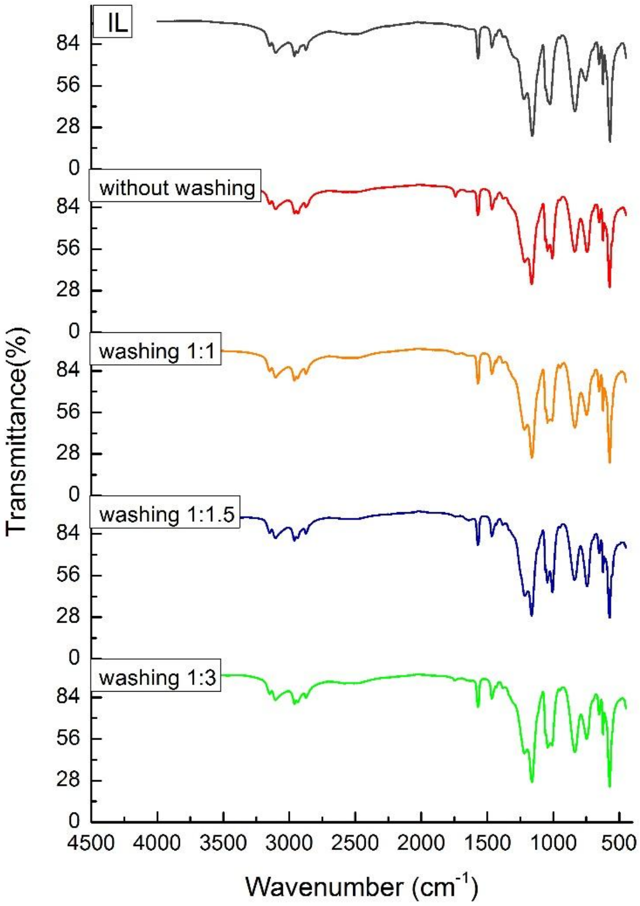


Figure 36. Spectra of the different process of washing to recoveries of the ionic liquid.

Secondly, different drying processes were tested, in which the first sample was dried for 5 h at 110 °C and the second sample was dried for 1 h at 110 °C and then for 15 h at 60 °C. After passing through these different processes, the samples were washed with water using the same mass ratio and finally dried. The samples were analyzed by FT-IR in order to determine their correlation with an original sample of [BMIM]HSO_4. These results are shown in Table 25.

Table 25. Results of different drying processes.

	Mass recovered (%)	**Correlation (%)**
Drying 1	95	96.1
Drying 2	95	86.2

With this it was possible to determine that the best IL recovery procedure involves a washing step with a sample/water mass ratio of 1:3, followed by a drying process during 5 h at 110 °C. Figure 37 shows the spectra of the recovered IL samples using the two different drying processes, obtained by FT-IR analysis.

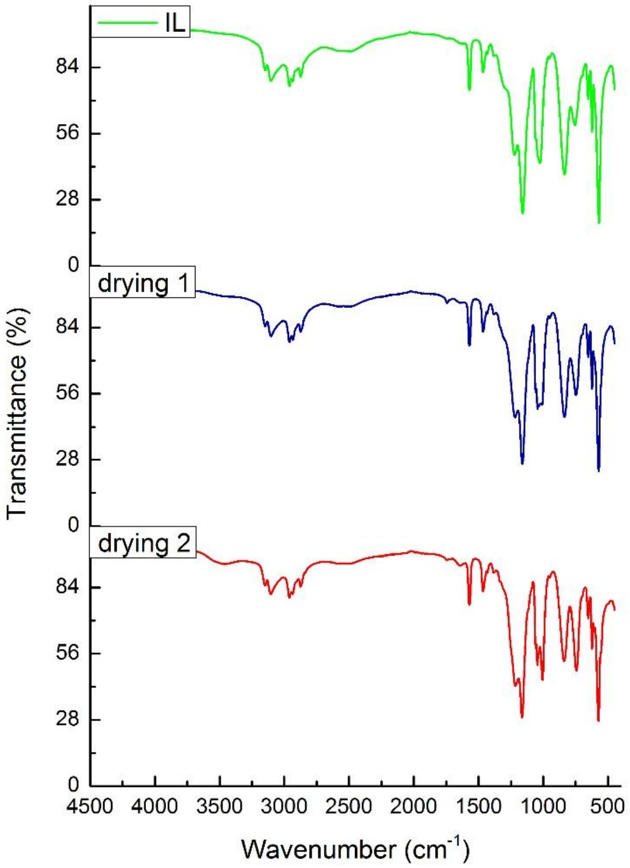


Figure 37. Spectra of the different process of drying to recoveries of the ionic liquid.

4.4.2 Process for recovering [BMIM]HSO_4 applying the proposed methodology

As proposed in the developed methodology, after the reaction of synthesis of biodiesel, the product is, firstly, introduced in test tubes for phase separation, for a period of approximately 40h at a temperature of 4 °C, and then for a period of approximately 20 min in the rotary centrifuge at 3000 rpm.

After separation, the aqueous and organic phases are placed in distinct and duly weighed vials. The aqueous phase goes through the proposed drying and washing process, which is characterized by a first drying step at 110 °C for 5 h and a second step of washing with water using a mass ratio of 1:3. This solution is then maintained at 4 °C for a period of 15 h for complete phase separation.

From this moment it is possible to separate the aqueous solution, which contains ionic liquid and water, from its residue, which possibly consists of organic matter. The solution composed of ionic liquid and water is sent to the oven for another 5 h at 110ºC to finally recover the ionic liquid.

Figure 38 illustrates all of the recovery steps.

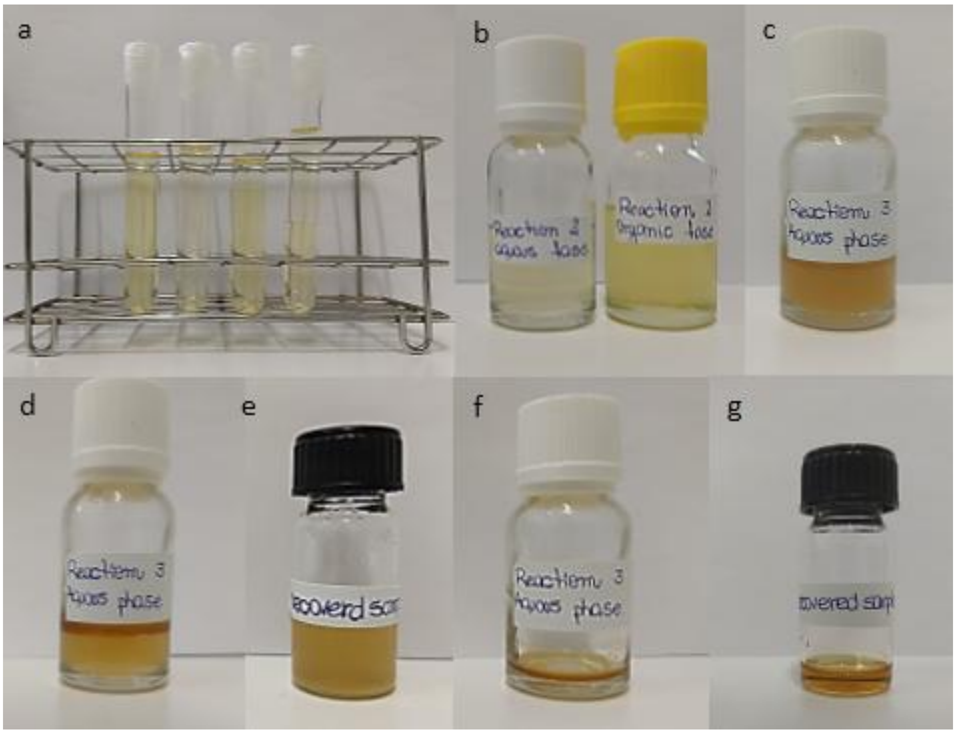


Figure 38. Ionic liquid recovery steps
a: phase separation in test tubes; **b:** aqueous and organic phase after separation; **c:** aqueous phase immediately after drying and washing; **d:** aqueous phase after separation; **e:** recovered sample; **f:** residue; **g:** recovered ionic liquid.

The first reaction was carried out with the introduction of 1.0410 g of [BMIM]HSO_4 as catalyst. After going through the entire recovery procedure, a new reaction was performed with the recovered IL, repeating the process during 5 reaction cycles. The initial and final masses, as well as the mass recovery percentage of trials 1 to 5 are shown in Table 26.

Table 26. Parameters for the recovery tests.

	Initial mass (g)	Final mass (g)	Mass recovered (%)
Reaction 1	1.0410	1.0130	97.3
Reaction 2	1.0130	0.9925	98.0
Reaction 3	0.9925	0.9558	96.3
Reaction 4	0.9558	0.9331	97.6
Reaction 5	0.9331	0.8938	95.8

It is necessary to point out that for each of the tests performed the mass of catalyst used at the beginning of the reaction corresponded to approximately 10% wt of the feedstock used, being indispensable to consider the gradual reduction of the mass of the simulated oil used in each reaction cycle.

Acidity reduction analysis for conversion estimation and FAME content were performed on the biodiesel produced in each of the five reactions. The results are shown in Figure 39 and Figure 40.

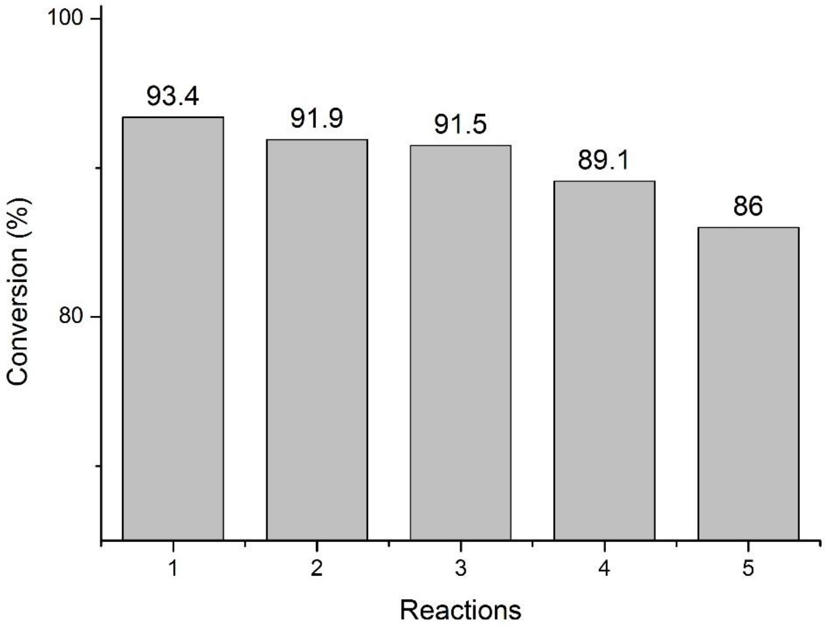


Figure 39. Conversion variation during the IL recovery cycles.

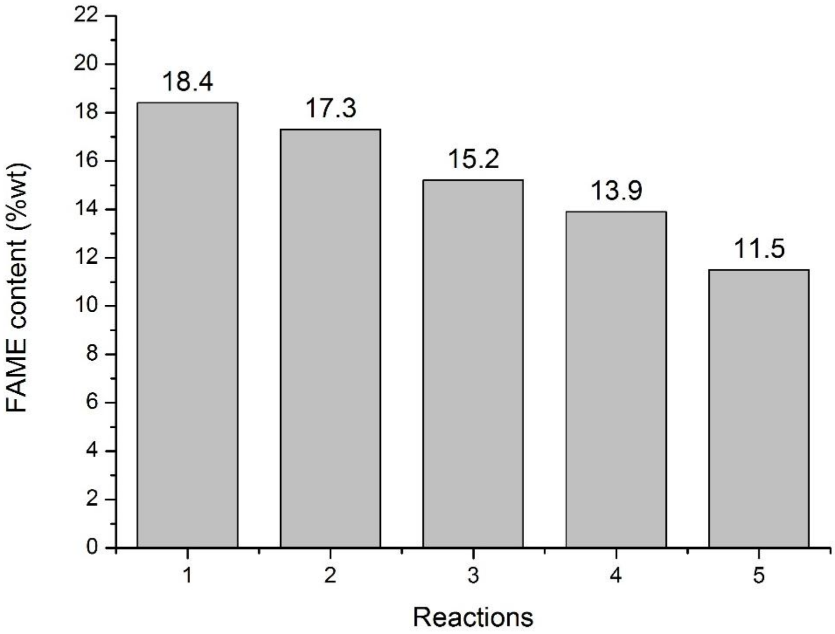


Figure 40. FAME content variation during the IL recovery cycles.

It is possible to observe that in the first three cycles the conversion decreased smoothly. However it is noticeable the occurrence of more abrupt decreases for the 4th and 5th cycle. When compared to the first cycle, the following cycles show decreases of 1.5%; 2.0%; 4.6% and 7.9%, respectively.

In the same way as the conversion calculated through the reduction of acidity, the FAME content in each of the tests has decreased, and the largest reduction was observed in the last one. When compared to the first cycle, the others had a decrease of 6.0%; 17.4%; 24.4% and 37.5%, respectively, which is a noticeable progression. This large decrease in FAME content is, also, due to the fact that at each cycle the mass of the feedstock used was reduced, relative to the mass of catalyst lost, thus having a constant catalyst dosage of 10 %wt.

After the fifth cycle, the recovered ionic liquid was subjected to FT-IR analysis to determine its purity and correlation with a sample of the ionic liquid not yet used. A 96.8% correlation was obtained between the samples, and it is possible to verify that after five reactions of biodiesel production the [BMIM]HSO_4 still has high purity.

Figure 41 shows the spectra with the unused IL and the IL after the fifth productive cycle.

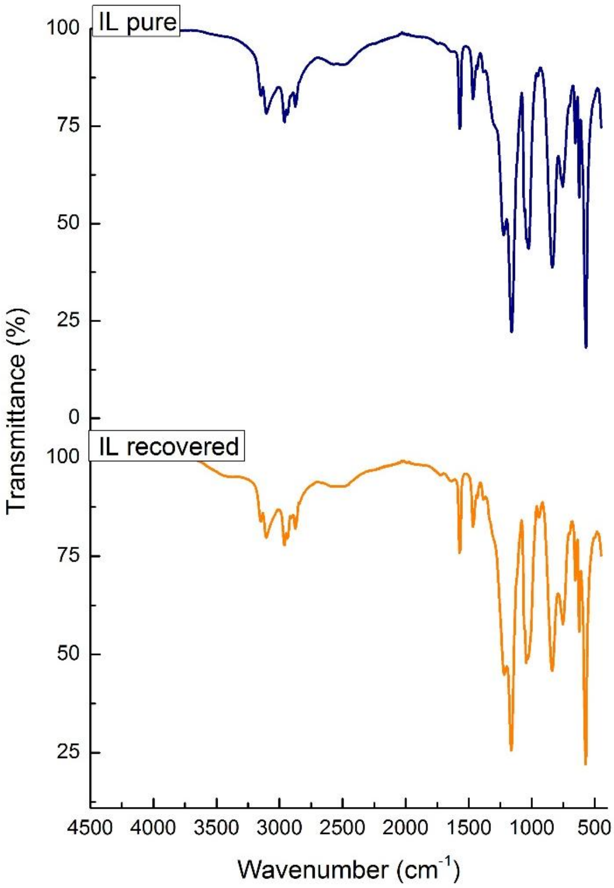


Figure 41. Spectra with the unused IL and the IL recovered.

When comparing these results with the results of the [BMIM]HSO_4 recovery studies mentioned in section 2.1.6 it is possible to verify that the proposed recovery method was efficient.

Fauzi and Amin (2013) [30] proposed an alternative process to recover this IL after the production of biodiesel by esterification reaction, through drying overnight at 105 °C. The authors performed five cycles with the catalyst. The oleic acid conversion and the methyl oleate yield were practically constant, 80.4% and 81.8% respectively.

Tadevosyan (2017) [34], studied the transesterification reaction and the respective phase separation, and proposed a two steps process involving drying the sample in an oven for one hour at 110 °C, followed by drying under vacuum for 12 to 15 hours at 60 ºC. There was recovery of the catalyst in 5 cycles, and the reaction yield decreased from 84.8% to 77.1%.

Sun *et al.* (2017) also proposed a recycling method of [BMIM]HSO_4. The aqueous phase was collected after filtration of algae and then dried under vacuum at 60

°C. The authors recovered the ionic liquid in 4 reaction cycles, reducing the yield from 95.28% to 81.23%.

It is important to point out that these authors mentioned only the effect of the recovery and reuse of the ionic liquid in the conversion, and not in the FAME content.

4.5 FT-IR qualitative analysis

Infrared spectrophotometry (FT-IR) was used to identify the chemical nature of some raw materials and the produced biodiesel, making it evident whether the conversion of free fatty acids to esters actually occurred. In Figure 42, the FTIR spectrum obtained with a sample of the waste cooking oil is presented.

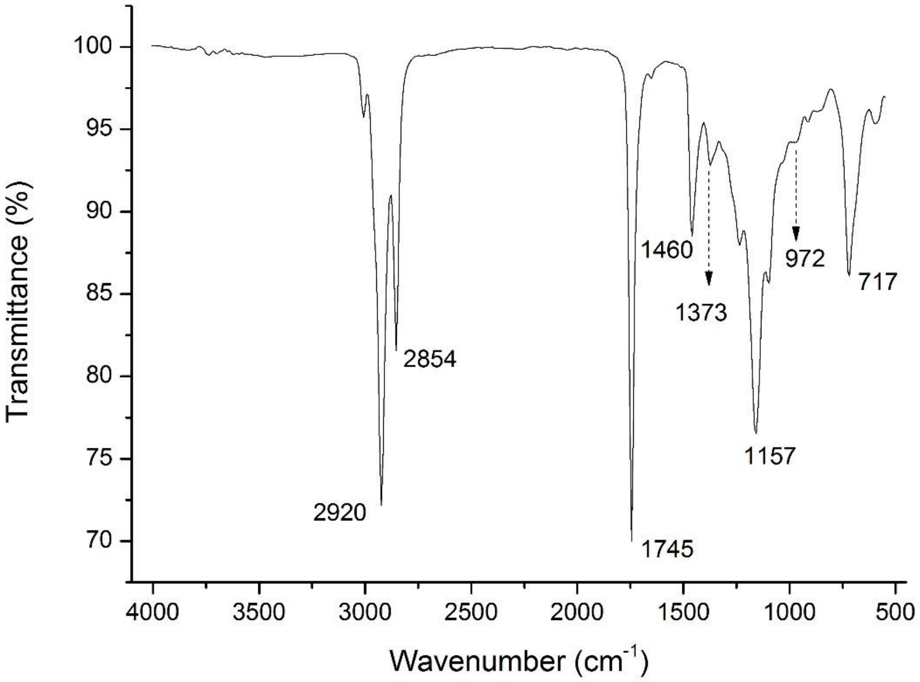


Figure 42. FT-IR spectrum of waste cooking oil.

The waste cooking oil is essentially composed of triglycerides, which are esters. The absorption characteristics of the ester are a strong absorption near 1740 cm^{-1} associated with the elongation of C=O, which in this case is represented by the strong bond at 1745 cm^{-1}, and the strong band near 1200 cm^{-1} to the asymmetric elongation of the CO bond, which is evident in the 1157 cm^{-1} band.

The bands at 2920 and 2855 cm^{-1} are again attributed to the elongation of aliphatic C-H bonds. The bands at 1460 and 1373 cm^{-1} are related to the deformation of CH_3 at methyl groups close to the carbonyl group, the one with the longer wavelength represents the asymmetric deformation and the shorter wavelength represents a symmetric deformation, respectively. The band at 972 cm^{-1} is attributed to flutter vibration of the CH_2, and the band at 717 cm^{-1} is attributed to the combined swing vibration of four or more CH_2 groups in an open chain [56].

Figure 43 shows the spectrum of oleic acid 90% (OA) used in the incorporation in WCO, for the simulation of the high acidity oil samples used in the reaction tests.

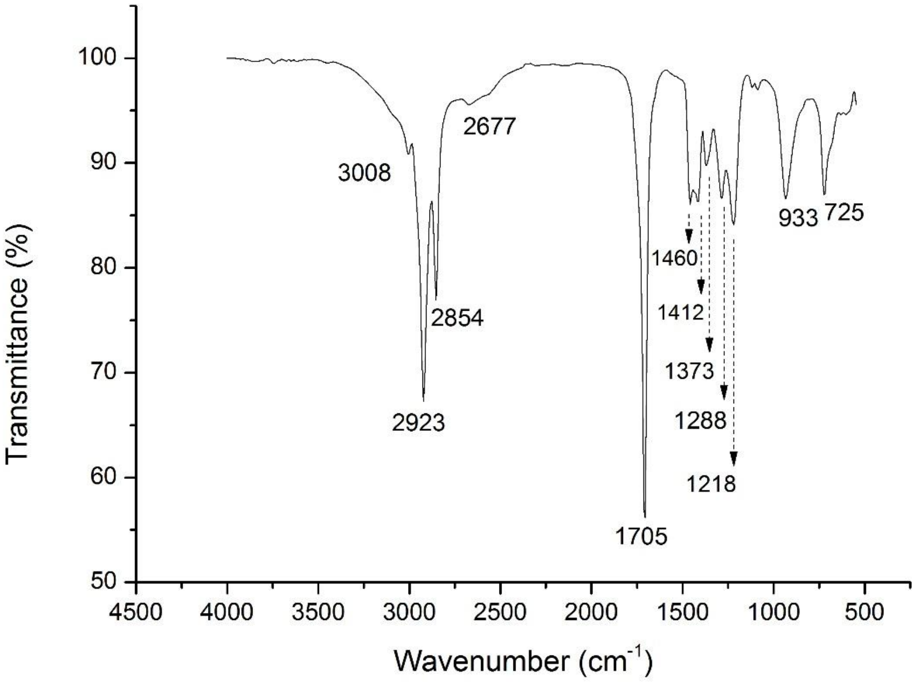


Figure 43. FT-IR spectrum of OA.

The broadband of 3300 to 2500 cm^{-1} and centered at 3008 cm^{-1} is a characteristic absorption attributed to acidic hydrogen and strongly bound, being characteristic of the carboxylic acids. The band at 2677 and 2550 cm^{-1} is also in this harmonic region and is a characteristic pattern of this group. The band at 2923 cm^{-1} that overlaps the broad band corresponding to the O-H bond is associated with the asymmetric elongation of aliphatic C-H bonds, whereas the band and 2854 cm^{-1}

is associated with the symmetrical elongation of aliphatic C-H bonds. The strongest band visible at 1705 cm^{-1} is attributed to elongation of the C=O bond of a dimer in the carboxylic acid, such as oleic acid. The 1460 cm^{-1} band is associated with the asymmetric deformation of CH_3 and the 1373 cm^{-1} band is associated with angular deformation of this group. The band at 1412 cm^{-1} is related to the CH_2 curve and the multiple weak bands at 1288 and 1218 cm^{-1} are related to oscillation vibrations of the same group in normal hydrocarbon chains. Both of these bands are related to elongation and folding in the COOH group, as a consequence of the combination of asymmetric O-C-O stretch and OH curve. The 933 cm^{-1} range is characteristic of dimeric oleic acid and results from an angular deformation outside the plane of the O-H bond. The band at 725 cm^{-1} is attributed to the combined balance of all CH_2 groups in the chain of four or more carbons [57,58].

On the other hand, Figure 44 shows the spectrum of the produced biodiesel.

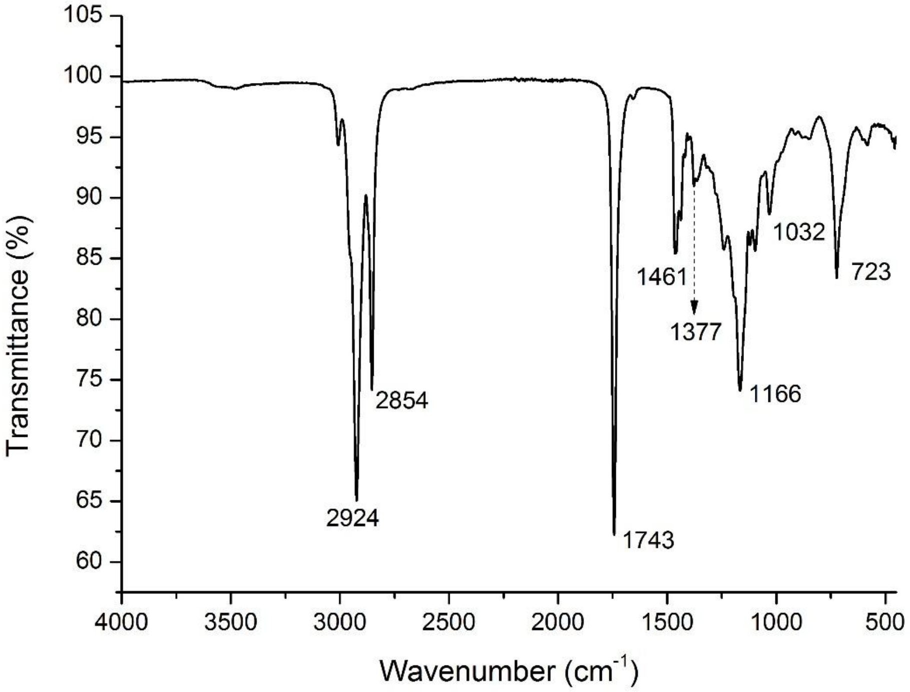


Figure 44. FT-IR spectrum of produced biodiesel.

The analyzed biodiesel sample was obtained under the following conditions: 65 °C, 10%wt catalyst, 8h, 1:20 molar ratio oil/MeOH, and 40%wt OA incorporation.

As shown in others spectra, the 2924 and 2854 cm^{-1} bands are also associated with asymmetric and symmetrical stretching of aliphatic C-H bonds, respectively. The bands at 1461 and 1377 cm^{-1} are related to the deformation of CH_3 at methyl groups near the carbonyl group, in an asymmetric and symmetrical manner, respectively. The 723 cm^{-1} band is associated with the swing motion of four or more CH_2 groups in an open chain. It is also noticeable the differences in this spectrum in relation to the raw materials, proving the conversion of FFA to FAME. The differences are: the disappearance of the 3000 cm^{-1} centered bandwidth, and the shift in C=O bond absorption band, now at 1743 cm^{-1}, which is a characteristic absorption of the C=O bond band in esters. It may also be noted that two or more bands related to the stretching vibration CO are present in the spectrum, in the region of 1300-1000 cm^{-1} which are characteristic of this group when connected to the carbonyl group. In this spectrum one can see the higher band at 1166 cm^{-1} and the lowest at 1032 cm^{-1} [57].

5. CONCLUSIONS

The main objective of this study was the production of biodiesel through the reaction of esterification/transesterification of a simulated oil, based in several mixtures of waste cooking oil and OA, catalyzed by the ionic liquid1-butyl-3-methylimidazolium hydrogen sulfate, [BMIM]HSO_4.

It is known that the reuse of waste cooking oil for the production of biodiesel has the potential to reduce the cost associated with the product, which makes it competitive with the petrochemical market. The characterization of the oil used in this study showed that it is similar to a sunflower oil, mainly composed of 43.4% of C18:2 (linoleic acid methyl ester), 37.2% of C18:1 (oleic acid methyl ester), 10% of C16:0 (palmitic acid methyl ester), 2.7% of C18:3n3 (linolenic acid methyl ester) and 1% of C18:0 (stearic acid methyl ester), in a weight basis.

The ionic liquid showed promising results for the production of biodiesel by the esterification reaction of the incorporated oleic acid, but it was not able to induce the transesterification reaction of triglycerides. Therefore, it is a valid alternative for the treatment of waste oils, by reducing their level of acidity and adding value to this product.

The experimental design allowed to understand how each factor (OA incorporation, oil/methanol molar ratio and reaction time) influences both conversion and FAMEs content of the biodiesel samples obtained when [BMIM]HSO_4 is used as a catalyst.

For both responses, conversion and FAME content, the most relevant factor was the incorporation of OA, followed by the reaction time and finally by oil/methanol molar ratio. There were defined the ideal conditions that led to the highest possible conversion and the highest possible FAME content. The ideal conditions for conversion were estimated at 20%wt OA incorporation; an oil/MeOH molar ratio of 1:20 and a reaction time of 8h leading to a conversion of 87.8%. The optimal condition, which leads to the highest FAME content of 37.6%wt, was estimated at 40%wt of OA incorporation; oil/MeOH molar ratio of 1:20 and a reaction time of 8h. It was also estimated the optimal condition for both responses, as 37.3%wt incorporation of OA; oil/MeOH molar ratio of 1:20 and a reaction time of 8h, which leads to a conversion of 82.2% and a FAME content of 35.6%wt.

The kinetic study allowed to evaluate the influence of the molar ratio of oil on the esterification reaction, showing that above a ratio of 1:25 the conversion remains unchanged for a period of 8 h. For molar ratios of 1:25; 1:30 and 1:40, 70% conversion was reached for the pre-determined time in all the experiments.

Then, it was possible to measure the activation energy of the esterification reaction catalyzed by ionic 1-butyl-3-methylimidazolium hydrogen sulfate by changing the reaction temperature, reaching a value of 52.2 kJ/mol. This activation energy value means that the reaction is influenced by the temperature, which reinforces the fact that the maximum conversions reached for a reaction time of 8 h and decrease as the temperature decreased, obtaining a maximum value of 70% for the temperature of 65 °C and 51% for 45 °C .

The proposed methodology for the recovery of the ionic liquid was efficient, being feasible until five consecutive cycles of reuse, leading to a decrease in conversion from 93.4 % to 86.9 % and the content of FAMEs initially measured in 18.4 %wt decreased to 11.5 %wt.

In conclusion, [BMIM]HSO_4, was not able to promote the transesterification reaction, but presented excellent results as a catalyst for the esterification reaction. Its use can be applied as a preliminary treatment for non-edible commercial oils with high FFA content, that is, acid oils. The preliminary treatment may increase the cost of biodiesel production, but recovery of ionic liquid is an advantage to reduce process costs.

5.1 Suggestions for future works

Some studies are still needed for a complete analysis of the suitability of 1-butyl-3-methylimidazolium hydrogen sulfate for biodiesel production. Suggestions for future work are:

- The study of the influence of the catalyst mass load, and the correspondent optimization analysis together with the other parameters, such as reaction temperature, molar ratio oil/MeOH, oleic acid incorporation and reaction time;

- The study of biodiesel production using a two-stage conversion process. The first stage with [BMIM]HSO_4 ionic liquid as a catalyst for the esterification of the FFAs present in the waste oil. The second stage in a consecutive reaction with a basic catalyst such as NaOH and KOH, for the promotion of the transesterification reaction;

- A more extensive study using alternative acidic ionic liquids for the production of biodiesel from waste cooking oils;

- The improvement of the recovery of [BMIM]HSO_4 IL with liquid-liquid extraction by screening a wide range of different organic solvents in which [BMIM]HSO_4 is soluble, such as n-hexane, dichloromethane and acetic anhydride.

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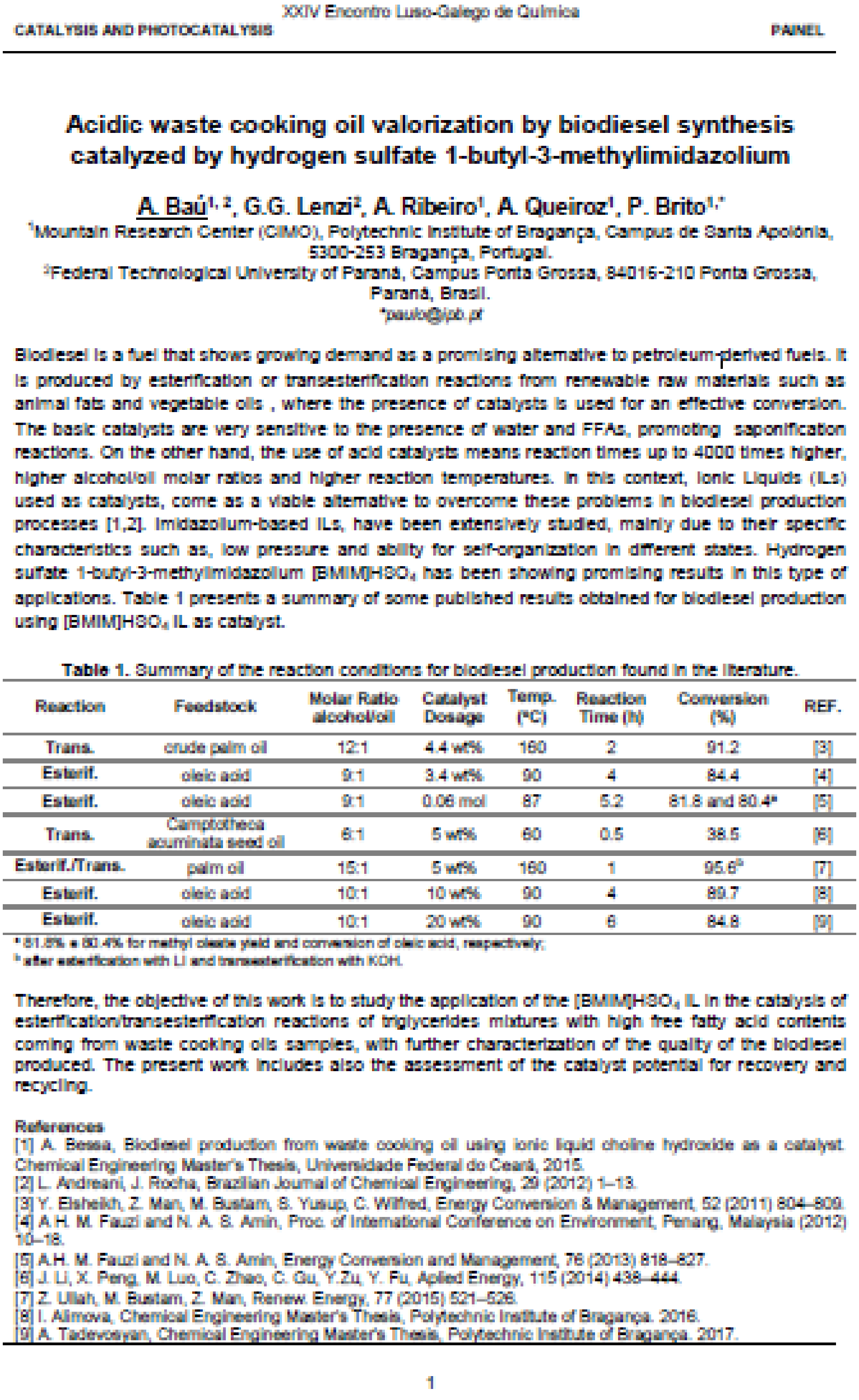
APPENDIX

A.1 – XXIV Encontro Luso Galego de Química, Porto, November 2018.



XXIV Encontro Luso-Galego de Química
CATALYSIS AND PHOTOCATALYSIS **PAINEL**

Acidic waste cooking oil valorization by biodiesel synthesis catalyzed by hydrogen sulfate 1-butyl-3-methylimidazolium

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Biodiesel is a fuel that shows growing demand as a promising alternative to petroleum-derived fuels. It is produced by esterification or transesterification reactions from renewable raw materials such as animal fats and vegetable oils , where the presence of catalysts is used for an effective conversion. The basic catalysts are very sensitive to the presence of water and FFAs, promoting saponification reactions. On the other hand, the use of acid catalysts means reaction times up to 4000 times higher, higher alcohol/oil molar ratios and higher reaction temperatures. In this context, Ionic Liquids (ILs) used as catalysts, come as a viable alternative to overcome these problems in biodiesel production processes [1,2]. Imidazolium-based ILs, have been extensively studied, mainly due to their specific characteristics such as, low pressure and ability for self-organization in different states. Hydrogen sulfate 1-butyl-3-methylimidazolium [BMIM]HSO_4 has been showing promising results in this type of applications. Table 1 presents a summary of some published results obtained for biodiesel production using [BMIM]HSO_4 IL as catalyst.

Table 1. Summary of the reaction conditions for biodiesel production found in the literature.

Reaction	Feedstock	Molar Ratio alcohol/oil	Catalyst Dosage	Temp. (°C)	Reaction Time (h)	Conversion (%)	REF.
Trans.	crude palm oil	12:1	4.4 wt%	160	2	91.2	[3]
Esterif.	oleic acid	9:1	3.4 wt%	90	4	84.4	[4]
Esterif.	oleic acid	9:1	0.06 mol	87	5.2	81.8 and 80.4^a	[5]
Trans.	Camptotheca acuminata seed oil	6:1	5 wt%	60	0.5	38.5	[6]
Esterif./Trans.	palm oil	15:1	5 wt%	160	1	95.6^b	[7]
Esterif.	oleic acid	10:1	10 wt%	90	4	89.7	[8]
Esterif.	oleic acid	10:1	20 wt%	90	6	84.8	[9]

^{a} 81.8% e 80.4% for methyl oleate yield and conversion of oleic acid, respectively;
^{b} after esterification with LI and transesterification with KOH.

Therefore, the objective of this work is to study the application of the [BMIM]HSO_4 IL in the catalysis of esterification/transesterification reactions of triglycerides mixtures with high free fatty acid contents coming from waste cooking oils samples, with further characterization of the quality of the biodiesel produced. The present work includes also the assessment of the catalyst potential for recovery and recycling.

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XXIV Encontro Luso Galego de

QUÍMICA

CERTIFICADO

Certifica-se que o(a) Senhor(a) **Ana Caroline Baú (A. Baú)**

apresentou o(a) Comunicação em Painel com título

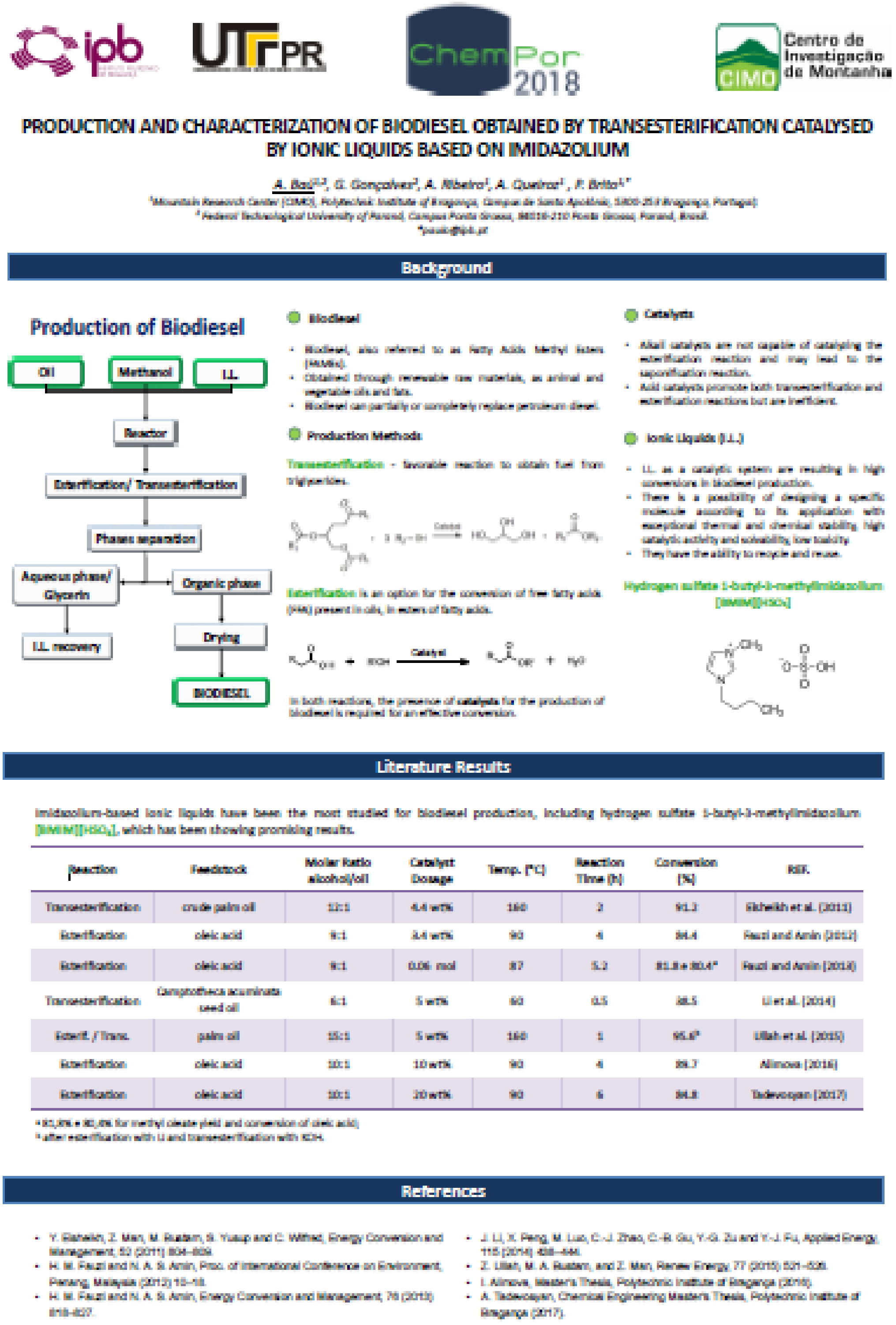
Acidic waste cooking oil valorization by biodiesel synthesis catalyzed by hydrogen sulfate 1-butyl-3-methylimidazolium

no XXIV Encontro Luso-Galego de Química (XXIV LGQ) na Faculdade de Ciências da Universidade do Porto, de 21 a 23 de Novembro de 2018

Pel´A Comissão Organizadora

Faculdade de Ciências da Universidade do Port,
23 de Novembro de 2018

A.2 – 13th International Chemical and Biological Engineering Conference (CHEMPOR 2018), Aveiro, October 2018.



PRODUCTION AND CHARACTERIZATION OF BIODIESEL OBTAINED BY TRANSESTERIFICATION CATALYSED BY IONIC LIQUIDS BASED ON IMIDAZOLIUM

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Background

Production of Biodiesel

Biodiesel

- Biodiesel, also referred to as Fatty Acids Methyl Esters (FAMEs).
- Obtained through renewable raw materials, as animal and vegetable oils and fats.
- Biodiesel can partially or completely replace petroleum diesel.

Production Methods

Transesterification - favorable reaction to obtain fuel from triglycerides.

Esterification is an option for the conversion of free fatty acids (FFA) present in oils, in esters of fatty acids.

In both reactions, the presence of **catalysts** for the production of biodiesel is required for an effective conversion.

Catalysts

- Alkali catalysts are not capable of catalyzing the esterification reaction and may lead to the saponification reaction.
- Acid catalysts promote both transesterification and esterification reactions but are inefficient.

Ionic Liquids (I.L.)

- I.L. as a catalytic system are resulting in high conversions in biodiesel production.
- There is a possibility of designing a specific molecule according to its application with exceptional thermal and chemical stability, high catalytic activity and solubility, low toxicity.
- They have the ability to recycle and reuse.

Hydrogen sulfate 1-butyl-3-methylimidazolium [BMIM][HSO₄]

Literature Results

Imidazolium-based ionic liquids have been the most studied for biodiesel production, including hydrogen sulfate 1-butyl-3-methylimidazolium [BMIM][HSO_4], which has been showing promising results.

Reaction	Feedstock	Molar Ratio alcohol/oil	Catalyst Dosage	Temp. (°C)	Reaction Time (h)	Conversion (%)	REF.
Transesterification	crude palm oil	12:1	4.4 wt%	160	2	91.2	Elsheikh et al. (2011)
Esterification	oleic acid	9:1	3.4 wt%	90	4	84.4	Fauzi and Amin (2012)
Esterification	oleic acid	9:1	0.06 mol	87	5.2	81.8 e 80.4[a]	Fauzi and Amin (2013)
Transesterification	Camptotheca acuminata seed oil	6:1	5 wt%	60	0.5	88.5	Li et al. (2014)
Esterif. / Trans.	palm oil	15:1	5 wt%	160	1	95.6[b]	Ullah et al. (2015)
Esterification	oleic acid	10:1	10 wt%	90	4	89.7	Alimova (2016)
Esterification	oleic acid	10:1	20 wt%	90	6	84.8	Tadevosyan (2017)

[a] 81,8% e 80,4% for methyl oleate yield and conversion of oleic acid;
[b] after esterification with IL and transesterification with KOH.

References

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CERTIFICATE

We certify that the abstract:

PRODUCTION AND CHARACTERIZATION OF BIODIESEL OBTAINED BY TRANSESTERIFICATION CATALYSED BY IONIC LIQUIDS BASED ON IMIDAZOLIUM

was presented as **Poster**, at the CHEMPOR 2018 Conference, occured between 2nd and 4th October 2018, in Aveiro - PORTUGAL.

Author(s): Ana Bau[1,2]; Giane Gonçalves[2]; Ana Queiroz[1]; Antonio Ribeiro[1]; Paulo Brito[1]

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Carlos Manuel Silva
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João Coutinho
Comissão Científica

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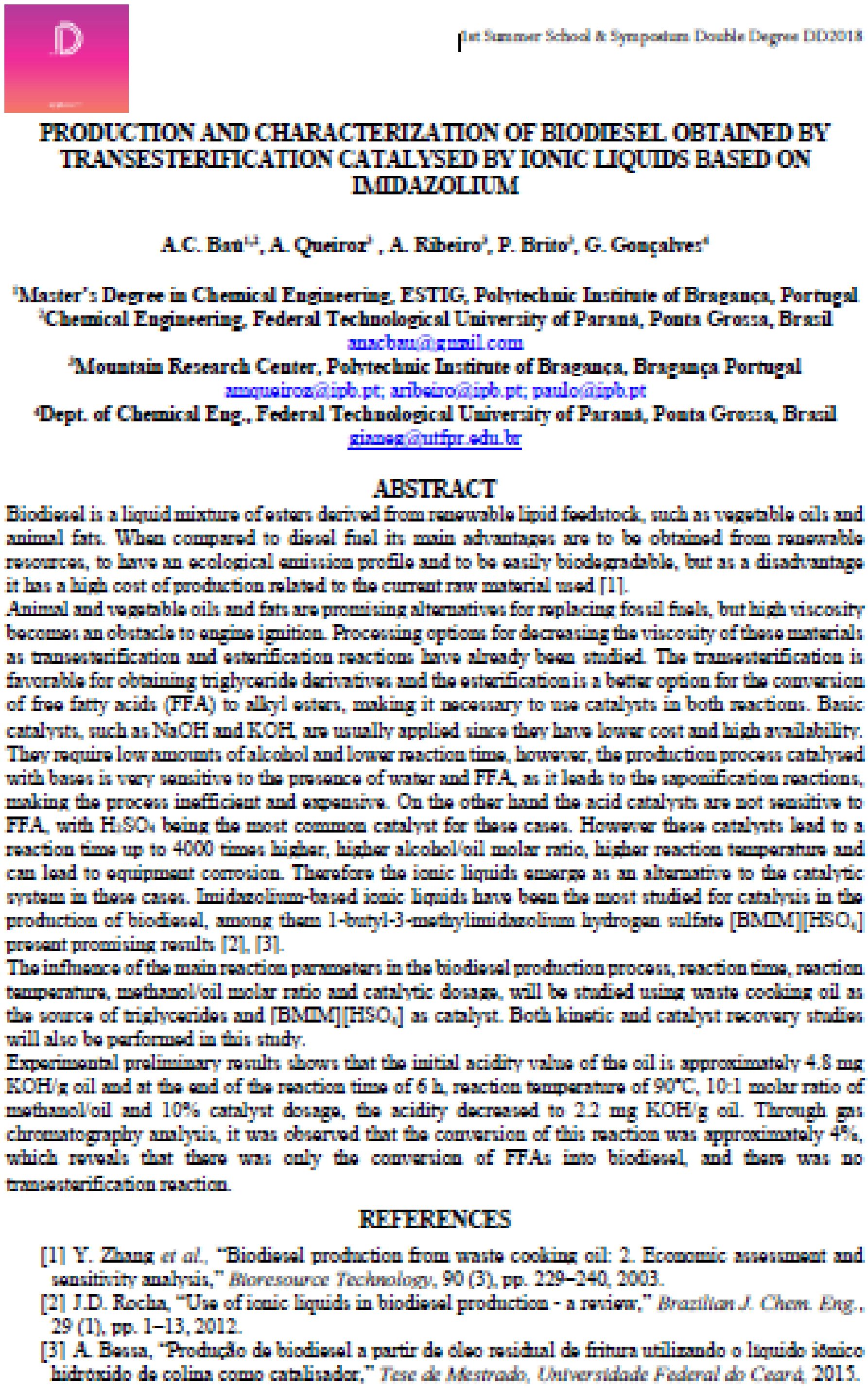
A.3 – 1st Double Diploma Summer School & Symposium 2018 (DD 2018), July 2018.



1st Summer School & Symposium Double Degree DD2018

PRODUCTION AND CHARACTERIZATION OF BIODIESEL OBTAINED BY TRANSESTERIFICATION CATALYSED BY IONIC LIQUIDS BASED ON IMIDAZOLIUM

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ABSTRACT

Biodiesel is a liquid mixture of esters derived from renewable lipid feedstock, such as vegetable oils and animal fats. When compared to diesel fuel its main advantages are to be obtained from renewable resources, to have an ecological emission profile and to be easily biodegradable, but as a disadvantage it has a high cost of production related to the current raw material used [1].

Animal and vegetable oils and fats are promising alternatives for replacing fossil fuels, but high viscosity becomes an obstacle to engine ignition. Processing options for decreasing the viscosity of these materials as transesterification and esterification reactions have already been studied. The transesterification is favorable for obtaining triglyceride derivatives and the esterification is a better option for the conversion of free fatty acids (FFA) to alkyl esters, making it necessary to use catalysts in both reactions. Basic catalysts, such as NaOH and KOH, are usually applied since they have lower cost and high availability. They require low amounts of alcohol and lower reaction time, however, the production process catalysed with bases is very sensitive to the presence of water and FFA, as it leads to the saponification reactions, making the process inefficient and expensive. On the other hand the acid catalysts are not sensitive to FFA, with H_2SO_4 being the most common catalyst for these cases. However these catalysts lead to a reaction time up to 4000 times higher, higher alcohol/oil molar ratio, higher reaction temperature and can lead to equipment corrosion. Therefore the ionic liquids emerge as an alternative to the catalytic system in these cases. Imidazolium-based ionic liquids have been the most studied for catalysis in the production of biodiesel, among them 1-butyl-3-methylimidazolium hydrogen sulfate [BMIM][HSO_4] present promising results [2], [3].

The influence of the main reaction parameters in the biodiesel production process, reaction time, reaction temperature, methanol/oil molar ratio and catalytic dosage, will be studied using waste cooking oil as the source of triglycerides and [BMIM][HSO_4] as catalyst. Both kinetic and catalyst recovery studies will also be performed in this study.

Experimental preliminary results shows that the initial acidity value of the oil is approximately 4.8 mg KOH/g oil and at the end of the reaction time of 6 h, reaction temperature of 90°C, 10:1 molar ratio of methanol/oil and 10% catalyst dosage, the acidity decreased to 2.2 mg KOH/g oil. Through gas chromatography analysis, it was observed that the conversion of this reaction was approximately 4%, which reveals that there was only the conversion of FFAs into biodiesel, and there was no transesterification reaction.

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2018

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ECTS Label 2011 – 2014

Escola de Verão & Simpósio de Dupla Diplomação 2018

DD 2018

3 a 6 de julho, Instituto Politécnico de Bragança

CERTIFICADO

Serve o presente documento para certificar que

Ana Caroline Baú,

da Universidade Tecnológica Federal do Paraná, Brasil e Escola Superior de Tecnologia e Gestão do Instituto Politécnico de Bragança, Portugal,

participou na 1ª Escola de Verão & Simpósio de Dupla Diplomação 2018 (DD 2018) que decorreu de 3 a 6 de julho no Instituto Politécnico de Bragança, Portugal, e apresentou a comunicação oral:

Production and characterization of biodiesel obtained by transesterification catalysed by ionic liquids based on imidazolium

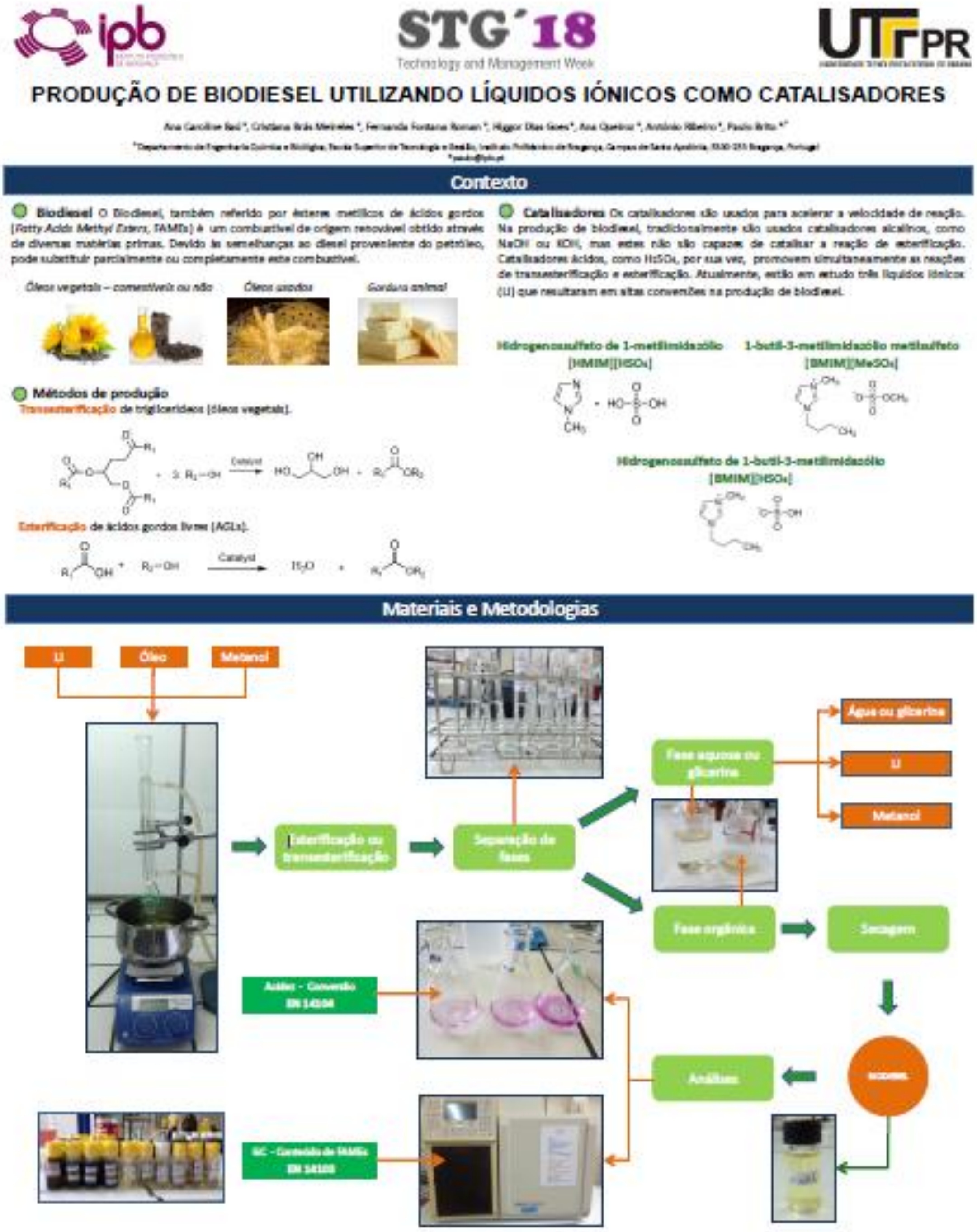
na **Sessão 2A – Engenharia Química, Engenharia Ambiente e Engenharia Alimentar**. Mais ainda, o referido trabalho foi **aceite para publicação nas Atas da 1ª Escola de Verão & Simpósio de Dupla Diplomação 2018**.

Bragança, 06 de julho de 2018.

João Paulo Pais de Almeida

João Paulo Almeida
Comissão Organizadora DD2018
Instituto Politécnico de Bragança

A.4 – Technology and Management Week (STG'18), May 2018.



STG´18
Technology and Management Week

PRODUÇÃO DE BIODIESEL UTILIZANDO LÍQUIDOS IÓNICOS COMO CATALISADORES

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Contexto

Biodiesel O Biodiesel, também referido por ésteres metílicos de ácidos gordos (*Fatty Acids Methyl Esters*, FAMEs) é um combustível de origem renovável obtido através de diversas matérias primas. Devido às semelhanças ao diesel proveniente do petróleo, pode substituir parcialmente ou completamente este combustível.

Óleos vegetais – comestíveis ou não *Óleos usados* *Gordura animal*

Métodos de produção

Transesterificação de triglicerídeos (óleos vegetais).

Esterificação de ácidos gordos livres (AGLs).

Catalisadores Os catalisadores são usados para acelerar a velocidade de reação. Na produção de biodiesel, tradicionalmente são usados catalisadores alcalinos, como NaOH ou KOH, mas estes não são capazes de catalisar a reação de esterificação. Catalisadores ácidos, como H_2SO_4, por sua vez, promovem simultaneamente as reações de transesterificação e esterificação. Atualmente, estão em estudo três líquidos iónicos (LI) que resultaram em altas conversões na produção de biodiesel.

Hidrogenossulfato de 1-metilimidazólio [HMIM][HSO_4]

1-butil-3-metilimidazólio metilsulfeto [BMIM][$MeSO_4$]

Hidrogenossulfato de 1-butil-3-metilimidazólio [BMIM][HSO_4]

Materiais e Metodologias