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ChemPor 2018

BOOK OF EXTENDED ABSTRACTS

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This volume contains the provisional version of the extended abstracts presented at the 13th International Chemical and Biological Engineering Conference (CHEMPOR 2018), held in Aveiro - Portugal, from the 2nd to the 4th of October, 2018.

University of Aveiro & Ordem dos Engenheiros

13th International Chemical and Biological Engineering Conference (CHEMPOR 2018)

Book of Extended Abstracts

Edited by:
João Araújo Pereira Coutinho
Carlos Manuel Silva
Inês Portugal
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SCIENTIFIC PROGRAM

Time	Tuesday, 2/10	Wednesday, 3/10	Thursday, 4/10
8:00 – 8:15	Registration		
8:15 – 8:30			
8:30 – 8:45			
8:45 – 9:00			
9:00 – 9:15		Plenary Lecture (PL3) Rajamani Krishna	Plenary Lecture (PL5) Gabriele Centi
9:15 – 9:30			
9:30 – 9:45	Welcome Session		
9:45 – 10:00			
10:00 – 10:15	Plenary Lecture (PL1) Nien-Hwa Linda Wang	O-BB07 O-EE01 O-IM03	O-RS11 O-EE10 O-BS05
10:15 – 10:30		O-BB08 O-EE02 O-IM04	O-RS12 O-EE11 O-BS06
10:30 – 10:45		O-BB09 O-EE03 O-IM05	O-RS13 O-EE12 O-BS07
10:45 – 11:00		O-BB10 O-EE04 O-IM06	O-RS14 O-EE13 O-BS08
11:00 – 11:15	Coffee-break	O-BB11 O-EE05 O-IM07	O-RS15 O-EE14 O-BS09
11:15 – 11:30		Coffee-break	Coffee-break
11:30 – 11:45	O-RS01 O-BS01 Bondalti		
11:45 – 12:00	O-RS02 O-BS02 O-MP01	O-BB12 O-EE06 O-ME01	Plenary Lecture (PL6) Nikolaos Hadjichristidis
12:00 – 12:15	O-RS03 O-BS03 O-MP02	O-BB13 O-EE07 O-ME02	
12:15 – 12:30	O-RS04 O-BS04 Prio	O-BB14 O-EE08 O-ME03	
12:30 – 12:45	O-RS05 O-BB01 O-IM01	O-BB15 O-EE09 O-ME04	
12:45 – 14:15	Lunch	Lunch	Lunch
14:15 – 14:30	Keynotes (KN1 and KN2) João Rocha, Rosa Quinta-Ferreira	Keynotes (KN3 and KN4) Adélio Mendes, José António Teixeira	Keynotes (KN5 and KN6) Maria Ascensão Reis, Ramesh Gardas
14:30 – 14:45			
14:45 – 15:00			
15:00 – 15:15	O-RS06 O-BB02 BB&G	Plenary Lecture (PL4) María José Cocero	O-RS16 O-EE15 O-IM11
15:15 – 15:30	O-RS07 O-BB03 O-MP03		O-RS17 O-EE16 O-IM12
15:30 – 15:45	O-RS08 O-BB04 BP		O-RS18 O-EE17 O-IM13
15:45 – 16:00	O-RS09 O-BB05 O-MP04		O-MP05 O-IM09 O-IM14
16:00 – 16:15	O-IM02 O-BB06 O-RS10	Poster Session and Coffee-break P-BB, P-RS, P-MP, P-ME	O-IM08 O-IM10 O-IM15
16:15 – 16:30	Plenary Lecture (PL2) Paul Christakopoulos		Awards and Closing Session
16:30 – 16:45			
16:45 – 17:00			Multibiorefinery Project Meeting (Coffee-break) CHEMPOR participants are welcome
17:00 – 17:15			
17:15 – 17:30	Formal Session with Minister of Economy	Bus to Vista Alegre	
17:30 – 17:45		Museum Visit	
17:45 – 18:00			
18:00 – 18:15	Poster Session and Coffee-break P-BS, P-IM, P-EE		
18:15 – 18:30			
18:30 – 18:45			
18:45 – 19:00			
19:00 – 19:15			
19:15 – 19:30			
19:30		Conference Dinner	

[PL] - Plenary Lecture
[KN] - Keynote Presentation
[RS] - Reaction and Separation Processes
[BS]- Biorefinery and Sustainability
[MP] - Modeling, Synthesis and Integration of Chemical Processes

[BB] - Biological Engineering and Biotechnology
[IM] - Innovative Materials and Applications
[EE] - Energy and Environment
[ME] - Multiscale and Multidisciplinary Engineering Education

Esterification process catalyzed by ionic liquids for fatty acid methyl esters production

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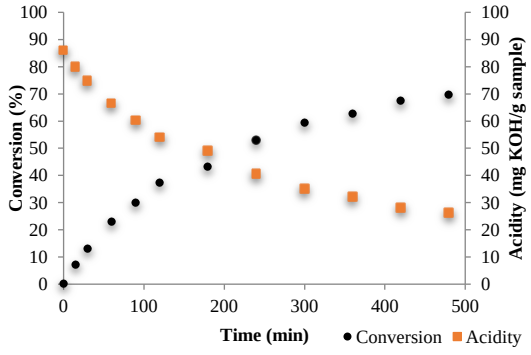

Due to the massive use of energy from non-renewable sources as well as to environmental problems it is important to find green alternatives. In this context the biodiesel production arises, as a possible diesel substitute which can be produced using basic or acid catalysts. Despite these traditional catalysts present high production yields, the problems that come from its use and the environmental impacts associated, result in the need for the search of more sustainable alternatives. The ionic liquids (IL) as possible catalysts represents an interesting alternative because IL are reusable and environmentally friendly. In present work, the main goal is to study biodiesel production using the ionic liquid 1-buthyl-3-methylimidazolium methyl sulfate [BMIM][$MeSO_4$] as catalyst, by the assessment of its kinetic activity. The results of kinetic study by the integral method, showed low activation energy of 5.16 kJ/mol and a pre-exponential factor (A) of 0.0624 $L^2.mol^{-2}.min^{-1}$.

Introduction

The high consumption of natural resources has increased the demand for renewable energy sources which have been gaining more importance to establish a world energy balance and to reduce existing energy needs. Thus, the demand for new renewable energy sources from biomass, such as biodiesel and bioethanol, are appointed as excellent options for substitution of fuels derived from petroleum. These types of energies can contribute to an improvement in different levels: environmental, social and economic. However, the development of its production processes requires improvements that are related to the implementation of profitable methods of production. So, the main goal is to establish biodiesel production using raw-materials such as non-edible oils and used cooking oils (UCO) using environmentally "friendly" catalysts, allowing the reduction of carbon dioxide emissions into the atmosphere.

The introduction of ionic liquids as catalysts in the production of biodiesel is a promising solution to solve the problems derived from the use of traditional catalysts, since the ionic liquids present properties which may give them the designation of "green" catalysts, namely the possibility of reuse without a significant loss in the yield of reaction.

With the goal of studying the ionic liquid 1-butyl-3-methylimidazolium methyl sulfate, [BMIM][$MeSO_4$] performance as a catalyst in the esterification reaction of oleic acid with methanol, it is important to establish a set of reaction parameters that define the optimal operational conditions of the process. These parameters are: reaction time, temperature, oleic acid/methanol molar ratio, and catalyst concentration in the reaction media.

However, in a first approach, a kinetic study was implemented in order to verify the sensitivity to temperature of the esterification reaction.

Material and Methods

Reagents. Oleic acid, tech 90% was used as obtained from ThermoFisher (Germany). The reagents obtained from Sigma Aldrich (Switzerland) were ionic liquid 1-buthyl-3-mehylimidazolium methyl. Methanol, ethanol and n-heptane were obtained from Fisher and anhydrous sodium sulfate was obtained from Carlo Erba (France). To prepare the solutions for the determination of acid value it was used hydrochloric acid from Fisher Chemical (United Kingdom), potassium hydroxide, diethyl ether and borax of Riedel-de-Haën (Germany). Acid-base indicators phenolphthalein and methyl red were obtained from Panreac (Spain) and Riedel-de-Haën (Germany), respectively.

Kinetic study of esterification reaction of oleic acid. The study of kinetic activity was performed in a flask with two nozzles, used as a 100 mL reactor, immersed in a paraffin bath. An automatic heating plate with magnetic stirring (VWR, model VMS-C4), equipped with a temperature sensor, and a reflux condenser were used. The needed quantities of ionic liquid, oleic acid and methanol were always added in this order into the reactor.

All kinetic studies of esterification reaction of oleic acid with methanol have been carried out using a time reaction of 8 hours. The catalyst quantity was 10% w/w and molar ratio oleic acid/methanol 1:10. Throughout the reaction, in pre-determined times (0, 15, 30, 60, 90, 120, 180, 240, 300, 360, 420 and 480 min), 1 mL of sample was removed from the flask using a micropipette and stored in 4 mL vials. The acidity value was determined according to the European Standard EN 14104 [1].The kinetic study was performed using four different reaction temperatures (60, 80, 100 and 110 °C) with the main goal of estimate experimentally the activity energy.

Results

Kinetic study of esterification reaction of oleic acid. The kinetic activity of the esterification reaction of oleic acid with methanol was studied using the [BMIM][$MeSO_4$] ionic liquid as catalyst.

In order to determine the order of the reaction, different measurements were carried out using different temperatures using 10% w/w of catalyst, 1:10 oleic acid/methanol molar ratio. For the determination of the order of reaction and the activation energy, the acid value, expressed in mg KOH/g biodiesel, (see Equation 1), was determined immediately after the sample collection in pre-determined times using the procedure according to European Standard EN14104 [1] using the following equation:

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

Where AV is the acid value, V_{KOH} is the volume of the KOH solution used in the titration, in mL, C_{KOH} is the concentration

of the standard KOH solution, in mol/L, MM_{KOH} is the molar mass of KOH, which is 56.1g/mol, and $m_{biodiesel}$ is the sample mass measured in g.
The conversion of oleic acid in percentage, was estimated by comparing the initial and final acidity values (see Equation 2). It was considered for the calculation of the initial acid value, the sample collected at time 0 min.

$$\text{Conversion}\ (\%) = \left(\frac{AV_0 - AV_1}{AV_0}\right) \times 100 \qquad (2)$$

Where AV_0 is the acidity for the oleic acid in initial instant and AV_1 is the final value acidity for a certain time, both in mg KOH/g sample.

Figures 1 and 2, show the evolution of acidity value and conversion with reaction time for different temperatures, respectively.

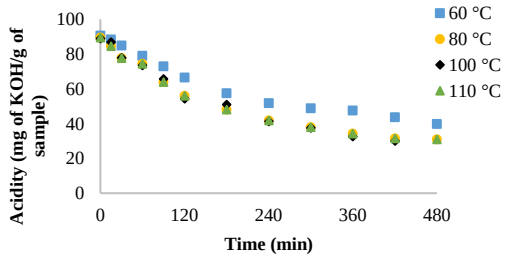

Figure 1. Effect of the time reaction in the acidity value using four different temperatures.

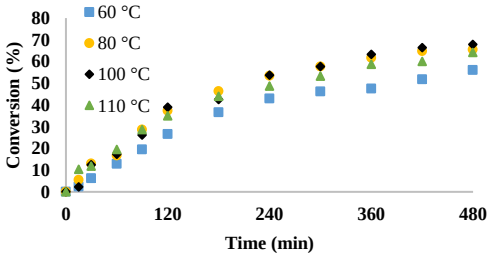

Figure 2. Effect of the time reaction in the conversion using four different temperatures.
Using these results, it was possible to estimate the order of reaction regarding to oleic acid. So, the integral method was applied for 0th, 1st, 2nd and 3rd order kinetics relating to oleic acid, for all temperatures. The results were studied for each reaction order and it was expected that if a particular order should be respected, the corresponding data would be distributed in a straight line. Afterwards, the regression coefficients (R^2) were compared and the order of reaction was selected taking account the highest correlation coefficient value attained. Arrhenius theory was used for calculation of activation energy, for the esterification of oleic acid using the previously referred ionic liquid. Equation 3 was used to represent a quantitative basis for the relationship between the activation energy, temperature and reaction rate constant.

$$k = Ae^{-E_a/RT} \qquad (3)$$

The logarithmic form of Equation 3 can be expressed as:

$$\ln k = \ln A - \frac{Ea}{R} \times \frac{1}{T} \qquad (4)$$

Where k is the reaction rate constant, A is the Arrhenius constant or pre-exponential constant, R is the universal gas constant ($kJ.mol^{-1}.K^{-1}$), T is the absolute temperature (K) and E_a is the activation energy (kJ/mol).
Fig. 3 shows the ln *k* values plotted against 1000/T, in order to determine the activation energy (E_a), as presented in Equation 4.

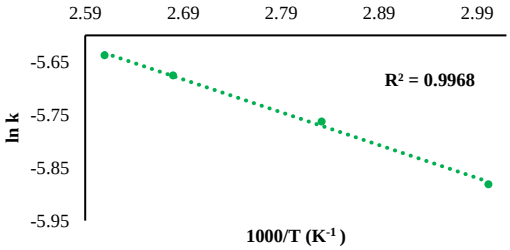

Figure 3. Arrhenius plot of the rate constant (ln k) versus the inverse of temperature (1000/T) for the esterification of oleic acid catalyzed by [BMIM][$MeSO_4$] ionic liquid.

The highest regression coefficient was obtained for the analysis considering a 2nd order kinetics for all temperatures, with a regression coefficient (R^2) of 0.9968. Therefore, the activation energy (E_a) and the pre-exponential factor (A) were estimated assuming the type of kinetics referred above. The obtained value for the activation energy (E_a) was 5.16 kJ/mol and the pre-exponential factor (A) was estimated at 0.0624 $L^2.mol^{-2}.min^{-1}$. Roman [2] presented a similar study using the IL 1-buthyl-3-methylimidazolium hydrogen sulfate ([HMIM][HSO_4]), and estimated the activation energy (E_a) as 6.80 kJ/mol and the pre-exponential factor as 0.0765 $L^2.mol^{-2}.min^{-1}$.

Conclusion

This work aims to study the use of [BMIM][$MeSO_4$] ionic liquid as a catalyst for the esterification reaction of oleic acid with methanol. The kinetic study showed a low activation energy of 5.16 kJ/mol, estimated by the application of the integral method, for a 2nd order kinetics relating to oleic acid. The relative low value found for the activation energy, indicates that the ionic liquid used in this study may be a viable catalyst for this type of reactions, showing a relative low sensitivity to temperature changes for the considered temperature range.

References

[1] European Committee for Standardization. EN 14104: Fat and oil derivates-Fatty Acid Methyl Esters (FAME) - Determination of acid value, 3 (2003) 1–14.
[2] F.F. Roman, Biodiesel production through esterification applying ionic liquids as catalysts, Master Thesis, Instituto Politécnico the Bragança, 2018.