XXII Encontro Luso-Galego Química

Optimization of biodiesel production through esterification catalysed by an acidic ionic liquid

Steliyana T. Yordanova, Ana Maria Queiroz, António Ribeiro, Paulo Brito*

Department of Chemical and Biological Technology, School of Technology and Management, Polytechnic Institute of Bragança

Campus de Santa Apolónia, 5300-253 Bragança, Portugal

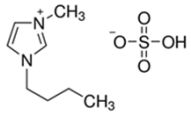
*paulo@ipb.pt

INSTITUTO POLITÉCNICO DE BRAGANÇA Escola Superior de Tecnologia e Gestão

Introduction

- Study of the performance of the acidic ***Ionic Liquid***, **1-butyl-3-methylimidazolium hydrogen sulfate** ([BMIM]HSO_4), as a catalyst for the esterification of a mix of fatty acids (mostly oleic acid) to the respective FAME's, using methanol.

Esterification reaction

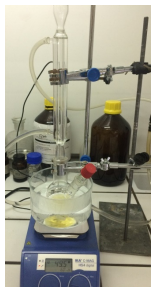


[BMIM][HSO_4]

- Multiple reaction batches were designed varying several operational parameters: **temperature**, **reaction time**, **oleic acid/methanol mole ratio** and **mass of catalyst**, in order to optimise the reaction yield.
- The prediction of the reaction yield was done using two indirect methods:
  - ❑ measuring the final product **acidity value** through volumetric titration,
  - ❑ assessing the total **FAME content** of the biodiesel product by Gas Chromatography (GC-FID).

Experimental Section

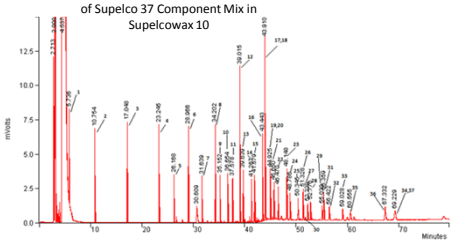
- ***Reaction***
  - Esterification takes place in a round flask where the required amounts of oleic acid, acidic catalyst and methanol are added, with reflux and temperature control, during the specified reaction time.
  - The product is cooled and decantates for 24 h, with the objective of separating the two phases: an organic phase (biodiesel) and an aqueous phase.



- ***Acidity Value***
  - Determination of the acidity value of the biodiesel samples is carried out through acid base volumetric titration with a KOH solution, using a 1:1 diethyl ether/ethanol mix as solvent.
- ***Gas Chromatography***
  - Analyzing the compounds in a commercial standard mix (37 FAME Mix: 47885-U SUPELCO) serves as a basis for comparison of the retention times of different compounds in biodiesel samples.
  - The analysis of the biodiesel samples, using the same operational conditions, allows the qualitative identification of the FAMEs present in the sample, and the estimation of the respective content by comparison of areas.

Gas Chromatograph Varian 3800GC equipped with flame ionization detector (FID)

Chromatogram with the content of FAMEs of Supelco 37 Component Mix in Supelcowax 10



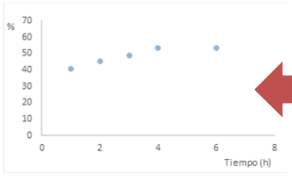
Parameter	Selected value
Reaction time	4 h
Reaction temperature	90 ºC
Mole ratio (OA/Met)[a]	1:10
weight % catalyst[b]	10%

[a] OA – oleic acid; Met – methanol
[b] relating to oleic acid weight

Results

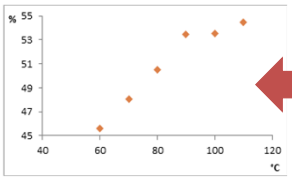
- *Optimization of the production of biodiesel*

Reaction time



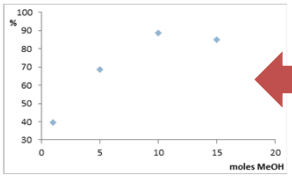
Nº	REACTIVOS	CONDICIONES	ACIDEZ INICIAL (mgKOH/g)	ACIDEZ FINAL (mgKOH/g)	CONVERSIÓN
t 1	A.O./MeOH 1:2 10% BMIMHSO4	1 h 80°C 300rpm	194,56	115,16	40,81%
t 2	A.O./MeOH 1:2 10% BMIMHSO4	2 h 80°C 300rpm	194,56	106,01	45,51%
t 3	A.O./MeOH 1:2 10% BMIMHSO4	3 h 80°C 300rpm	194,56	99,20	49,01%
t 4	A.O./MeOH 1:2 10% BMIMHSO4	4 h 80°C 300rpm	194,56	91,01	53,22%
t 5	A.O./MeOH 1:2 10% BMIMHSO4	6 h 80°C 300rpm	194,56	90,98	53,24%

Reaction temperature



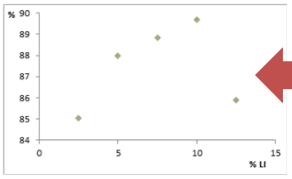
Nº	REACTIVOS	CONDICIONES	ACIDEZ INICIAL (mgKOH/g)	ACIDEZ FINAL (mgKOH/g)	CONVERSIÓN
T 1	A.O./MeOH 1:2 10% BMIMHSO4	60°C 4 h 300rpm	184,29	105,80	45,63%
T 2	A.O./MeOH 1:2 10% BMIMHSO4	70°C 4 h 300rpm	184,29	101,00	48,07%
T 3	A.O./MeOH 1:2 10% BMIMHSO4	80°C 4 h 300rpm	194,56	96,30	50,49%
T 4	A.O./MeOH 1:2 10% BMIMHSO4	90°C 4 h 300rpm	194,56	90,60	53,44%
T 5	A.O./MeOH 1:2 10% BMIMHSO4	100°C 4 h 300rpm	184,29	90,40	53,52%
T 6	A.O./MeOH 1:2 10% BMIMHSO4	110°C 4 h 300rpm	184,29	88,00	54,50%

Mole Ratio Oleic Acid/Methanol



Nº	REACTIVOS	CONDICIONES	ACIDEZ INICIAL (mgKOH/g)	ACIDEZ FINAL (mgKOH/g)	CONVERSIÓN
M 1	A.O./MeOH 1:1 10% BMIMHSO4	4 h 90°C 300rpm	194,56	117,10	39,79%
M 2	A.O./MeOH 1:5 10% BMIMHSO4	4 h 90°C 300rpm	194,56	61,00	68,64%
M 3	A.O./MeOH 1:10 10% BMIMHSO4	4 h 90°C 300rpm	194,56	20,10	88,69%
M 4	A.O./MeOH 1:15 10% BMIMHSO4	4 h 90°C 300rpm	194,56	29,50	84,82%

Catalyst %w

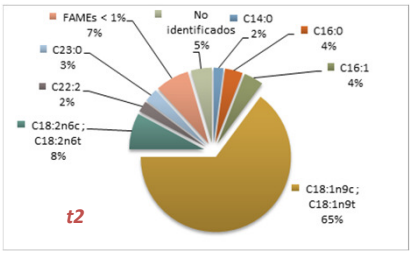


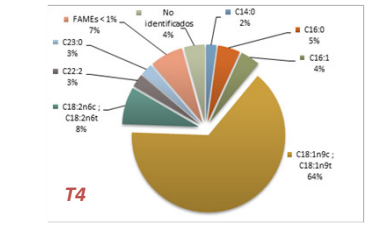
Nº	REACTIVOS	CONDICIONES	ACIDEZ INICIAL (mgKOH/g)	ACIDEZ FINAL (mgKOH/g)	CONVERSIÓN
LI 1	A.O./MeOH 1:10 2,5% BMIMHSO4	4 h 90°C 300rpm	194,56	29,10	85,03%
LI 2	A.O./MeOH 1:10 5% BMIMHSO4	4 h 90°C 300rpm	194,56	21,40	88,00%
LI 3	A.O./MeOH 1:10 7,5% BMIMHSO4	4 h 90°C 300rpm	194,56	21,70	88,84%
LI 4	A.O./MeOH 1:10 10% BMIMHSO4	4 h 90°C 300rpm	194,56	20,10	89,69%
LI 5	A.O./MeOH 1:2 12,5% BMIMHSO4	4 h 90°C 300rpm	194,56	27,50	85,88%

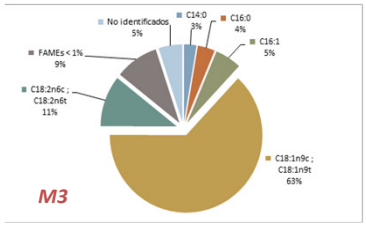
Optimised parameters

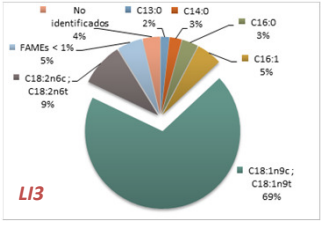
- Reaction yields reach values as high as 90%, and the total weight content of identified FAME's in the biodiesel product is 95-98%.
- The reaction of esterification in the presence of the ionic liquid 1-butyl-3-methyl imidazolium hydrogen sulfate is feasible for the production of biodiesel, but the yields are somewhat lower than those obtained by commonly used catalysts.
- Ionic liquid [BMIM]HSO_4 proves to be a promising catalyst for esterification reactions, and a potential alternative for biodiesel production.

- *Sample characterisation*









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