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

***C. Meireles*[1], *A. Queiroz*[1], *A. Ribeiro*[1], *P. Brito*[1,*]**

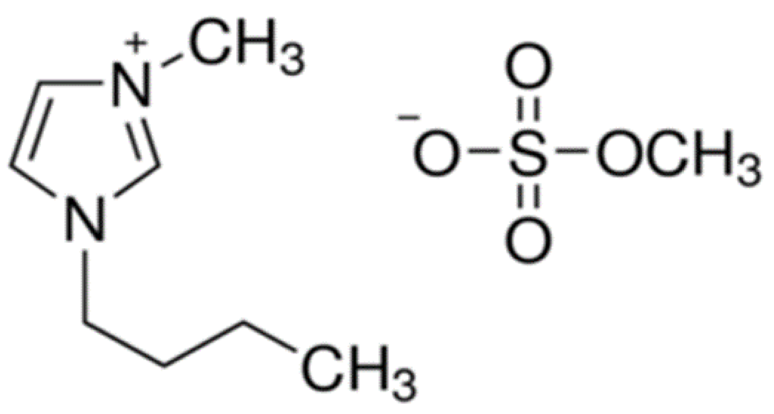
[1]Mountain Research Center (CIMO), Polytechnic Institute of Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal. *paulo@ipb.pt

Introduction

Biodiesel is a mixture of fatty acid methyl esters (FAMEs), prepared from vegetable oils and animal fats through esterification of free fatty acids (FFAs) and/or through transesterification of triglycerides, that arises as a **possible diesel substitute**. It can be produced using **basic or acid catalysts**. However, these traditional catalysts present problems, so there is a need for the searching of more sustainable alternative catalysts. The **ionic liquids (ILs)** are molten salts which exist in liquid state at temperature below 100°C and as catalysts are an **interesting alternative** to the traditional catalysts because **ILs can be reusable and are environmentally friendly.**

The **kinetics of the esterification** reaction of **oleic acid** with **methanol** was studied using **[BMIM][MeSO$_4$]** ionic liquid as catalyst.

In order to establish the evolution of the reaction, different experiments were carried out at different temperatures using **10% w/w of catalyst** and **1:10 oleic acid/methanol molar ratio**.



1-buthyl-3-methyl imidazolium methyl sulfate

The **evolution of the reaction with time** was determined by monitoring the **acidity value** of the reaction mix, expressed in mg KOH/g biodiesel, immediately after the sampling at predetermined times, using the procedure according to European Standard EN14104 [1].

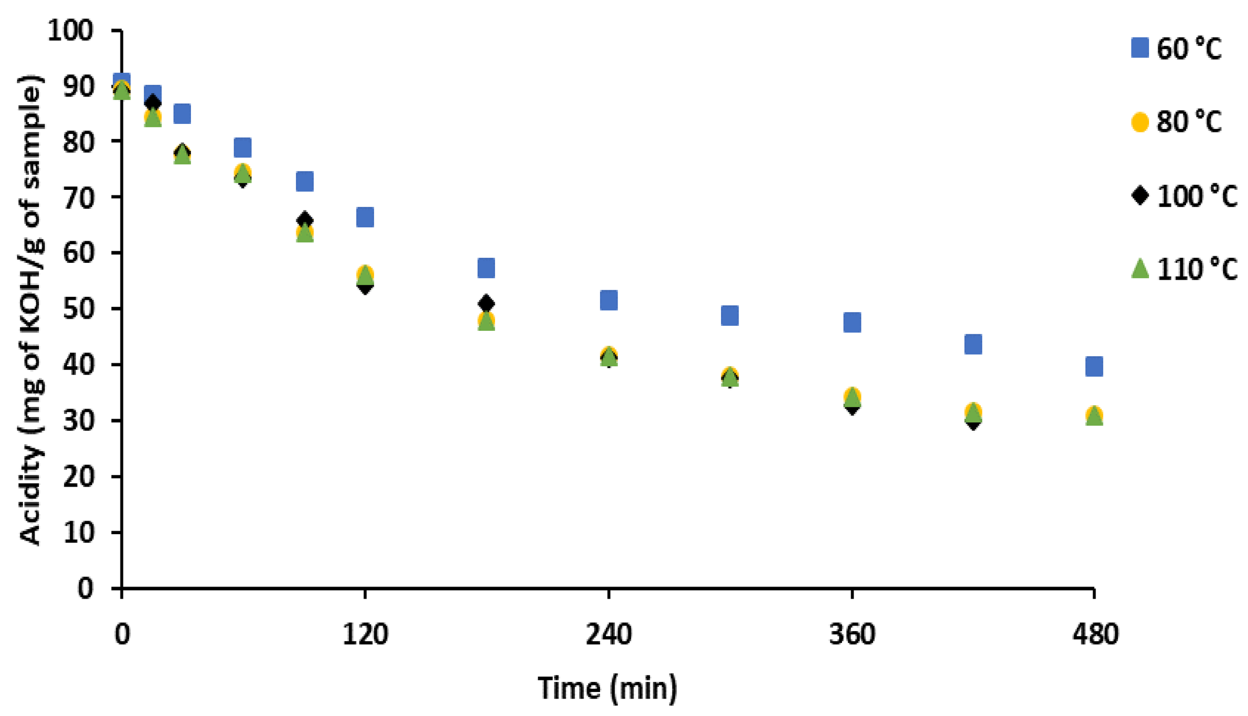


Figure 1-Evolution of acidity value with reaction time for different temperatures.

The **conversion** of oleic acid in percentage was estimated by comparing the initial and final acidity values of the reaction mix.

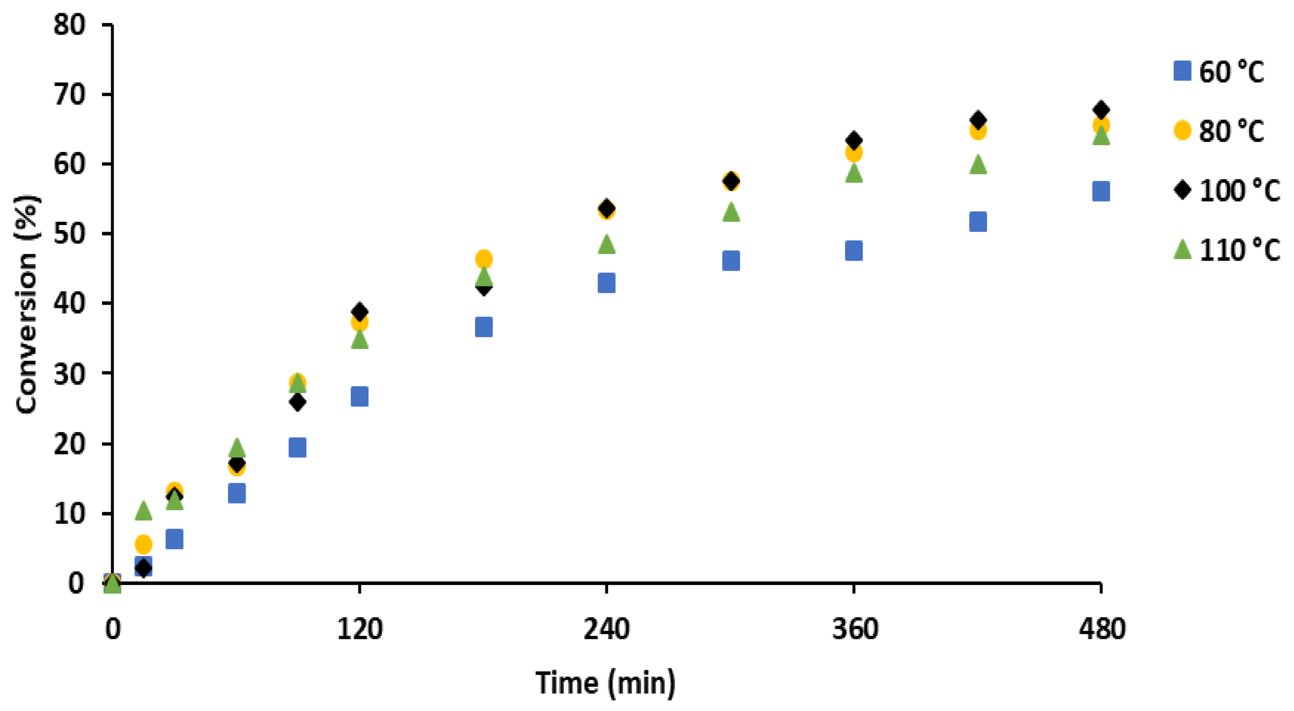
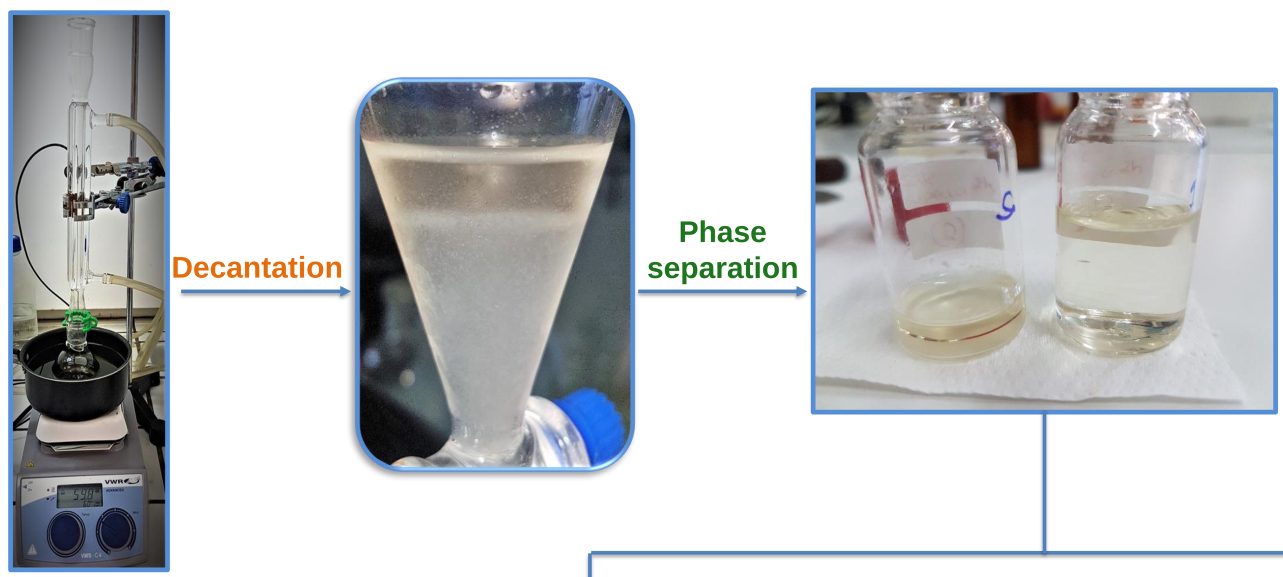
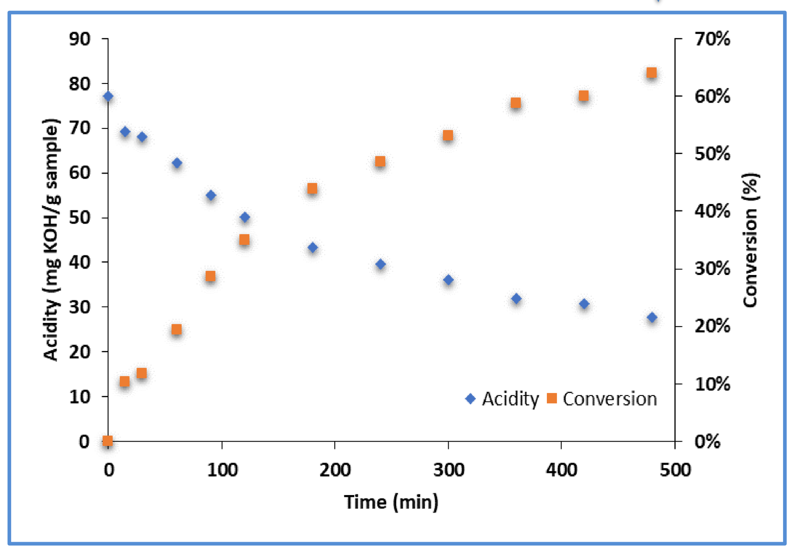
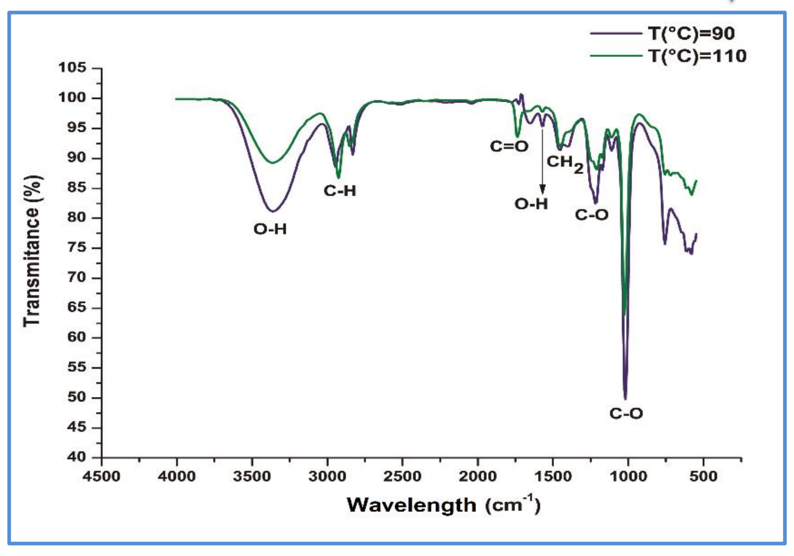


Figure 2- Evolution of conversion of oleic acid with reaction time for different temperatures.







Using the results of acidity and conversion, it was possible to estimate the **order of reaction** regarding to oleic acid.

The **integral method** was applied for **0th, 1st, 2nd and 3rd order kinetics** relating to oleic acid, for several temperatures.

Arrhenius equation for a selected **2nd order kinetics** was used for the estimation of the **activation energy** for the esterification of oleic acid using the previously referred ionic liquid.

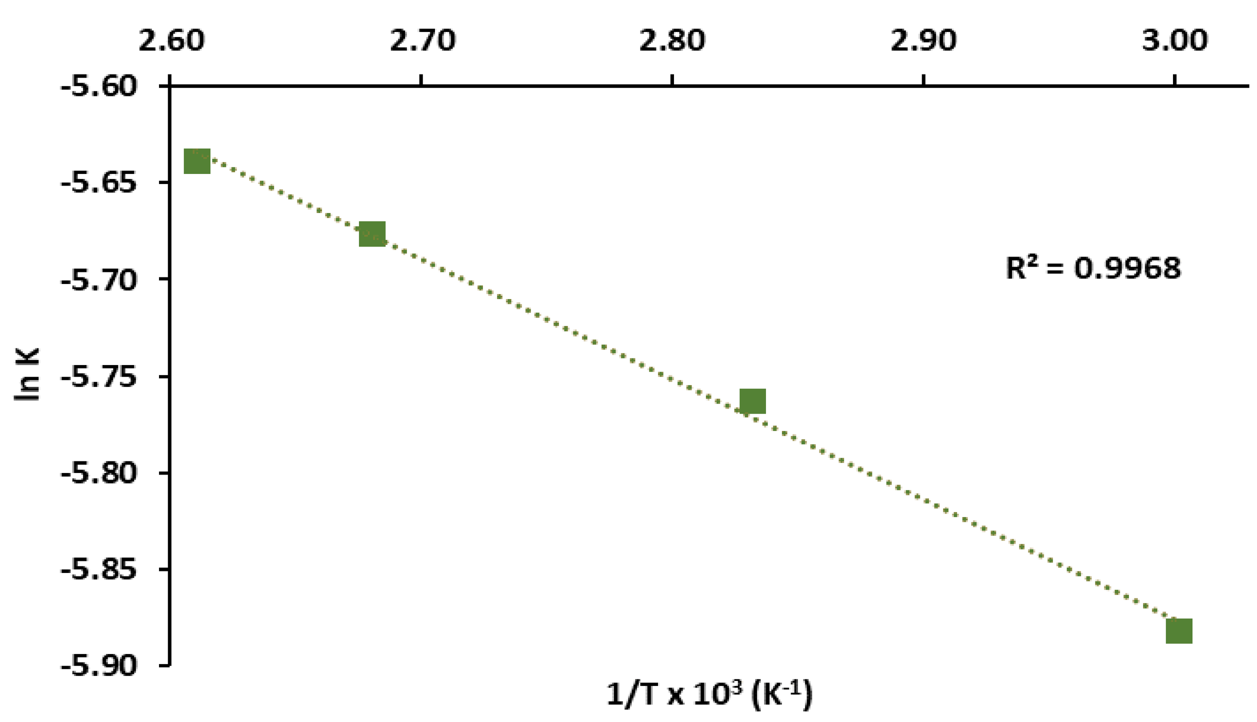


Figure 3- Graphic of ln k plotted against 1/T×10^3, in order to determine the activation energy (Ea).

The results obtained and their comparison with a previous published work are presented in following table.
Roman presented a similar study using **1-buthyl-3-methylimidazolium hydrogen sulfate,** [HMIM][HSO$_4$], as catalyst [2] .

Ionic liquid (LI)	Activation Energy (Ea) (kJ/mol)	Pre-exponential factor (A) (L^2.mol^{-2}.min^{-1})	Order	Reference
[BMIM][MeSO4]	5.16	0.0624	2nd	-
[HMIM][HSO$_4$]	6.80	0.0765	3rd	[2]

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] Roman, F.F., Biodiesel production through esterification applying ionic liquids as catalysts, Master Thesis, Instituto Politécnico de Bragança, 2018.