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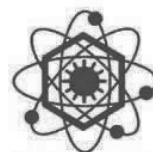
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Valorization of used cooking oils through ionic liquid catalyzed biodiesel conversion processes

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The search for alternative technologies to fossil fuel-based energy sources is a recent trend. One possible solution is to use biodiesel as a diesel substitute, reducing environmental impacts such as pollutant emissions. Biodiesel consists of a mixture of long chain fatty acid alkyl esters and is produced by converting vegetable oils or animal fats by transesterification reactions [1].

Due to the high cost of the usual raw material, there is a need to reduce the final price of biodiesel. Thus, oil sources that are not in competition with the food market, such as residual cooking oils, are used. However, these oils show high levels of free fatty acids, which can bring problems to the classic biodiesel production process, alkaline transesterification. To overcome these problems, ionic liquids (IL) can be used as catalysts, since they also promote esterification reactions of free fatty acids to biodiesel. Furthermore, ionic liquids present a few advantages, related to their recoverability and reusability, as well as the environmental and safety perspectives [1].

The objective of this work is to study the production of biodiesel by applying 1-methylimidazolium hydrogen sulfate IL ([HMIM][HSO₄]) as a catalyst in esterification/transesterification reactions with methanol in samples of high acidity residual vegetable oils. Additionally, the study of the IL recovery procedure will be carried out, with the evaluation of the maximum number of recovery cycles that can be performed without significant loss of reaction yield.

The following operational conditions were established for each reaction/recovery cycle: reaction time of 4 hours, temperature of 65°C, molar ratio 1:10 of oleic acid/methanol, and 10%wt. of IL charge relating to oleic acid. After the synthesis, the biodiesel acidity and the reaction conversion in terms of acidity decrease were determined by volumetric titration of the light biodiesel organic phase with potassium hydroxide (KOH) solution. Also, the FAME (fatty acid methyl esters) content of the biodiesel sample was quantified by gas chromatography (GC-FID). The IL recovery was done by drying the aqueous heavy phase at 110°C, followed by washing it with distilled water in a 1:3 mass ratio, separation of the IL phase, and a second drying step at 110°C [2]. The assessment of the quality of the recovered IL was done by Fourier Transform Infrared spectroscopy (FTIR), specifically through the measurement of the correlation between the recovered IL and the initial IL spectra.

The results obtained are presented in Table 1. Reaction 1 was performed with the commercial IL and the subsequent reactions were carried out using the IL samples recovered from the previous reaction cycle. Despite the use of the recovered ionic liquid, the conversion remained relatively high, with only a slight decrease. The correlation between the initial IL and the recovered IL was 99,15%, showing that the recovery method is efficient.

Table 1 – Experimental results obtained.

Reaction	Conversion (%)	IL Recovery (%wt.)
1	81,18	73,97
2	79,84	84,16
3	79,45	76,35
4	78,08	74,65

References [1] Z. Ullah, M. A. Bustam, Z. Man, Renewable Energy, 77 (2015) 521-526. [2] A. Baú, G. G. Lenzi, A. Ribeiro, A. Queiroz, P. Brito, Acidic waste cooking oil valorization by biodiesel synthesis catalysed by hydrogen sulfate 1-butyl-3-methylimidazolium, XXIV Encontro Luso-Galego de Química, CAT20, Porto, 21-23 november 2018.