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

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Recently, there is an increasing interest in the development of alternative technologies to the oil economy, based on renewable energy sources. A possible solution is a biofuel for compression-ignition or diesel engines, obtained from fat-rich biomass. Therefore, a wide variety of raw materials can be used for the production of biodiesel, ranging from waste oils to edible commercial oils.

Biodiesel is chemically composed by a mix of fatty acid methyl esters (FAME's), and it is usually produced by transesterification of triglycerides, from vegetable oils and animal fats, in the presence of homogeneous or heterogeneous catalysts. However, alkali catalysts which provide high yields for the production of biodiesel in relatively mild conditions require previous neutralization of the oils. In fact, the use of high acidic raw materials may introduce operational problems, especially when resorting to second generation triglyceride sources. This type of raw materials, like waste cooking oils, do not compete with the food market, but usually feature high levels of free fatty acids (FFA's), which may introduce complications in the classic production process of biodiesel, through alkaline transesterification. Thus, these problems can be partially prevented by the use of alternative acidic or basic catalysts, such as ionic liquids (IL's) that also mediate esterification reactions of FFA's to FAME's.

An increased interest in the application of IL's in multiple fields has been observed lately, mainly as solvents [1] and catalysts [2-4] to a wide variety of reaction and/or separation systems. In this work, it is presented a study of the performance of the acidic IL, 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO₄), as a catalyst for the esterification of a mix of fatty acids (mostly oleic acid) to the respective FAME's, using methanol.

Multiple reaction batches were designed varying several operational parameters: temperature, reaction time, oleic acid/methanol mole ratio and mass of catalyst, in order to optimize the reaction yield. The prediction of the reaction yield was done using two indirect methods: measuring the final product acidic value through volumetric titration and assessing the total FAME content of the biodiesel product by Gas Chromatography (GC-FID). The GC-FID analysis made possible the identification and quantification of the several FAME's present in the produced biodiesel.

Using the conditions described above the 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 optimized process conditions which allow the obtaining of higher reaction yields are summarized in Table 1. Thus, it is concluded that the ionic liquid [BMIM]HSO₄ proves to be a promising catalyst for esterification reactions, and a potential alternative for biodiesel production.

Table 1. Optimized reaction conditions for esterification

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

^a OA – oleic acid; Met – methanol

^b relating to oleic acid weight

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