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Zinc carboxylic salts used as catalyst in the biodiesel synthesis by esterification and transesterification: Study of the stability in the reaction medium

Deborath M. Reinoso, Daniel E. Damiani, Gabriela M. Tonetto *

Planta Piloto de Ingeniería Química PLAPIQUI (UNS – CONICET), Camino "La Carrindanga" Km 7, CC 717, CP 8000 Bahía Blanca, Argentina

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ABSTRACT

Biodiesel is produced by the catalytic transesterification of renewable sources such as vegetable oils and animal fats. It is an attractive alternative to diesel fuel because of its environmental benefits.

In this work, the transesterification of soybean oil with methanol using zinc carboxylic salts as Lewis acid catalysts was studied. The esterification of fatty acids was also researched. In both reactions, the stability of the catalyst in the reaction medium was examined.

Zinc carboxylic salts of different chain lengths, $Zn(C_nH_{2n+1}COO)_2$ with $n = 1$, 11, 15, and 17, and $Zn(C_{17}H_{33}COO)_2$ (zinc(II) acetate, laurate, palmitate, stearate and oleate, respectively) were prepared and characterized by X-ray diffraction, FTIR spectrometry and thermogravimetric analysis.

The Zn salts were tested in the transesterification of soybean oil at 100 °C for 2 h. They presented oil conversions between 88 and 94% with fatty acid methyl ester (FAME) yields between 71 and 74%, and they were stable in three consecutive tests. Zn acetate was not stable. The salts transformed into Zn glycerolate at 140 °C in the reaction medium (zinc laurate, palmitate, and stearate only partially).

It was observed that, in the presence of fatty acids, the carboxylates of the salts were gradually exchanged for the acid to be esterified. With oleic acid, this process was completed at 60 °C for all the $Zn(C_nH_{2n+1}COO)_2$ salts.

Zinc laurate, palmitate and stearate are crystalline solids, but soluble in the reaction medium at 100 °C, and they recrystallize rapidly at room temperature, presenting certain advantages as regards decreasing mass transfer resistance during reaction, and easy separation and recovery from reaction medium.

1. Introduction

The sustainable diversification of energy sources is the new industrial challenge. Renewable energies make up the industrial sector with the greatest growth in the world. In Argentina, biodiesel exports reached almost 1.7 million tons in 2011 for a value of approximately USD 2000 million, representing an increase of 29% compared to the previous year [1].

Biodiesel fuel, defined as fatty acid methyl or ethyl ester (FAME in the first case), is produced from biological sources such as vegetable oils and animal fats. FAME has become an attractive alternative fuel source because it is biodegradable and non-toxic, and its combustion generates less SO_X, CO, un-burnt-carbons, and particulates.

Almost all biodiesel is produced by transesterification of triglycerides of refined oils by homogeneous base catalysis (NaOH and $NaOCH_3$) [2,3] due to its low cost and high product yield. However, catalysts of this kind have the disadvantage of reacting with free fatty acids (FFAs) present in the raw material or fatty acids (FAs) produced by hydrolysis of the glyceride when water is present, generating soap. This undesirable sub-product makes difficult the separation and purification of biodiesel, and decreases the process yield. For these reasons, homogeneous base catalysts require expensive feedstocks with low levels of FFAs and water, or pretreatments of the raw material.

A homogeneous acid-catalyzed esterification stage, prior to transesterification, converts the FFAs into methyl or ethyl esters (depending on the alcohol used), allowing the use of cheaper raw materials to produce biodiesel.

Strong liquid acid catalysts are less active than base catalysts, but they can simultaneously catalyze esterification and transesterification reactions. So far, for acid-catalyzed systems, sulfuric acid has been the most investigated catalyst, but other acids such as HCl, BF_3, H_3PO_4, and organic sulfonic acids, have also been used by different researchers [4].

* Corresponding author. Fax: +54 291 4861600.
E-mail address: gtonetto@plapiqui.edu.ar (G.M. Tonetto).

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