Simultaneous Transesterification and Esterification to Biodiesel Using Zinc Oxide Based Catalyst

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Introduction

Biodiesel is a mixture of fatty acid esters which can be produced from vegetable oils or animal fats with methanol. A conventional operation usually uses strong basic or acidic solutions (i.e. NaOH, KOH and H_2SO_4) as catalyst and food-grade vegetable oils as raw material. These homogeneous catalysts are quite sensitive to free fatty acids (FFA) and water in the oil feedstocks and alcohols. FFA reacts with the basic catalyst (NaOH, KOH) and forms soaps. This soap formation complicates the glycerol separation, and drastically reduces the methyl ester yield. Water in the feedstock leads to hydrolysis of oils and fatty acid methyl esters (FAME) in the presence of strong basic or acidic catalysts. Thus, some inexpensive oils, such as crude vegetable oils, waste cooking oil, and rendered animal fats, which generally contain a high content of FFA and water, cannot utilize homogeneous catalysts directly. Recently, a two-step method was reported to using waste or unrefined oils as feedstock to decrease the production cost of biodiesel [1]. It firstly esterified FFA with methanol in the presence of H_2SO_4, then transesterified oil with methanol in the presence of NaOH. However, this production process is long and highly corrosive.

Previously, Yan et al. [2] reported that supported CaO catalysts directly catalyzed the reaction of some crude oils into biodiesel when water content in the oils was less than 2 (wt) % and FFA content less than 3.5 (wt) %. However, further increases of FFA and water content in oils could inhibit the transesterification. The mechanism for the improved tolerance to water and FFA of this type of catalysts was not fully elucidated.

In this study, a single-step method was developed for biodiesel production using waste or unrefined oils as feedstock based on a series of heterogeneous zinc and lanthanum mixed oxides. The reaction mechanism for transesterification and esterification were suggested.

Materials and Methods

A homogeneous-coprecipitation method was used to prepare zinc oxide based catalysts (Zn10La0, Zn1La1, Zn3La1, Zn9La1, Zn0La10). Catalysts were characterized by XRD, XPS, SEM and EDS measurements. Catalytic transesterification and esterification were conducted in a stainless steel stirred reactor (Parr 4575 HT/HP Reactor).

Results and Discussion

XRD results (Figure 1) show that Zn3La1 is a mixture of ZnO, La_2CO_5 and LaOOH phases. And the average crystal size of ZnO is about 17.1 nm. Using Zn3La1 catalyst, 96 % yield of FAME within 3 hours was obtained even with crude palm oil, crude soybean oil, waste cooking oil, food-grade soybean oil with 3 % water and 5 % oleic acid addition (Figure 2). Effects of free fatty acids (FFA) and water on biodiesel-formation reactions were investigated. Simultaneous transesterification of oil and esterification of FFA while minimum hydrolysis of oil and biodiesel reactions were founded during this process. Effects of metal oxide molar ratio, free fatty acids (FFA) and water content in feedstock, molar ratio of methanol and oil, and reaction temperature on the yield of biodiesel were also investigated.

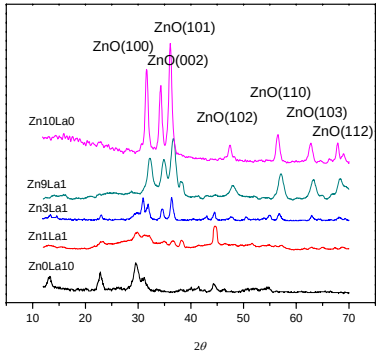

Figure 1. XRD patterns of pure and mixed zinc and lanthanum mixed metal oxides.

Significance

This class of catalysts can directly utilize waste or unrefined oils and it provides a potential to decreases the production cost and feedstock cost of biodiesel.

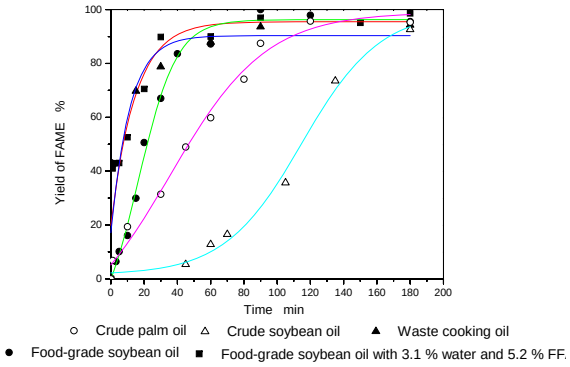

Figure 2. FAME yield of crude palm oil, crude soybean oil, waste cooking oil, food-grade soybean oil and food-grade soybean oil with 3.1 % water and 5.2 % oleic acid addition.

References

1. Ngo H.L., Zafiropoulos N.A., Foglia T. A., *Energy & Fuels* 626, 22 (2008).
2. Yan S.L., Lu H.F., Liang B., *Energy & Fuels*, 646, 22 (2007)