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Acidity reduction of enzymatic biodiesel using alkaline washing

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ABSTRACT

The aim of this communication is to report the reduction of biodiesel acidity by wet washing using aqueous/methanol NaOH solutions. For this purpose, some assays were carried out, varying temperature, methanol concentration, molar ratio of NaOH to FFA and the amount of NaOH solution, with results expressed in terms of final acidity and process yield. It is shown that 35 °C, 1 wt% of methanol, 1 NaOH:FFA molar ratio (i.e., 1 eqv, the stoichiometric relation), and 3 wt% of base solution in relation to crude biodiesel, resulting in a final FFA content of 0.19 wt% and around 96% of product yield.

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1. Introduction

Biodiesel, a renewable substitute/additive for diesel fuel, has been shown as a good alternative to reduce carcinogenic compound emissions [1] and greenhouse effect [2–5]. The use of liquid lipases for FAME production together with unrefined, less expensive, high FFA, lower-grade oils and fats would result in a dramatic reduction of the overall costs of enzyme-catalyzed biodiesel production [6]. On the other hand, biodiesel produced through liquid lipases, for example using Eversa® lipase (from Novozymes), leads inherently to a relative high acid product, usually with a free fatty acid (FFA) content around 3 wt% plus the presence of monoglycerides, diglycerides and triglycerides (and, obviously, free glycerin) generally above the specification [7,8].

After production, biodiesel is purified and dried to meet the parameters specified by standard specifications [9,10]. Several techniques have been studied for biodiesel purification, such as the use of hydrophilic hydrogels [11], ultrafiltration membranes [12], dry cold washing with cellulose and starch [13], neutralization processes with sodium hydroxide [14], neutral or acid wet and dry washing, membrane extraction, precipitation, complexation, simultaneous ion-exchange and precipitation as well as simultaneous biodiesel synthesis and purification [15] and Magnesol® and ion-exchange resins [2,16,17].

The wet washing process for biodiesel purification is far the widely applied process to remove impurities and it consists basically in successive washings with deionized water in order to remove impurities like methanol, free fatty acids (FFA), soaps and glycerol. Nevertheless, such method has some disadvantages like increasing in production time, product losses, large amounts of water required (for each liter of biodiesel, about 10 L of wastewater is produced), possible formation of FFA by hydrolysis of esters in presence of water, formation of soaps and the need of drying the washed product for removal of water traces [3,18,19].

Compared to dry washing techniques, wet washing using a base solution is considered a much simpler and effective method of biodiesel purification and presents lower running costs [19]. Besides, there is a lack of information about the chemical composition of ion-exchange resins and large scale use is still incipient in the biodiesel industry.

In this context, wet washing using sodium hydroxide to reduce FFA coming from the enzymatic (free-enzyme) biodiesel production of FAME seems to be a safer and robust strategy to reach the restringing specification of 0.25 wt% FFA in the final product. As no previous study was found in the open literature dedicated to such

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relevant step, this work reports new results of alkaline washing of enzymatic biodiesel trough a new approach making use of aqueous and methanol solutions of NaOH, aiming at reducing the FFA content in the final product with the compromise of minimum FAME losses.

2. Experimental

2.1. Materials

Distilled water, methanol (Vetec, 99.9%), sodium hydroxide (Vetec, 99%) and phenolphthalein were used in the tests. Enzymatic biodiesel was produced in orbital shaker using refined soybean oil, following the procedure given elsewhere [20]. The main characteristic of the FAME produced is: monoglycerides (MAG), diglycerides (DAG) and triglycerides (TAG) content of 0.430 wt%, 0.750 wt% and 0.230 wt%, respectively, 0.116 wt% of water and 3.94 wt% FFA.

2.2. Experimental procedure

2.2.1. Alkaline washing

The process of biodiesel purification by alkaline washing was carried out using crude biodiesel, water, methanol and sodium hydroxide. First, crude biodiesel (100 g) was weighed and placed in an orbital shaker (Tecnal model TE-4200) at 250 rpm with predetermined temperatures (35, 45, 55 and 65 °C). After 10 min, a NaOH solution was prepared using the NaOH to FFA equivalent ratio shown in Table 1, then was mixed with methanol (1.0 or 3.0 g), added to the biodiesel samples and allowed to react for 20 min under continuous agitation. Such reaction time was determined after preliminary tests and was verified to be more than sufficient to complete reaction, as this occurs very fast. Afterwards, an aliquot of 14 mL was taken from each sample and centrifuged for 10 min at 5000 rpm at room temperature. After centrifugation, the supernatant was carefully separated and used for measurements of acidity and product losses.

Temperature range (values within the interval of 35–65 °C) was chosen based on literature [14,21], with lower values so as to avoid biodiesel losses and soap formation. Methanol was used to prevent backward hydrolysis reaction whereas the molar ratio of NaOH to FFA and the amount of alkaline solution added to crude biodiesel samples were varied seeking improved acidity reduction while minimizing product losses [22].

2.2.2. Determination of alkaline washing yield

After centrifugation, the supernatant, mostly composed of methyl esters, was collected using a pipette and weighed in a high precision scale (Ohaus model AR2140, 0.1 mg precision, 210.0 g capacity). The process yield of alkaline washing was determined in terms of final weight of the supernatant phase by the weight of crude biodiesel charged.

2.2.3. Acidity determination

The determination of free fatty acids content in sample solution was carried by titration with KOH, following the IUPAC 2.201 method. The solution acidity was determined according to the following equation:

$$FFA(wt\%) = \frac{V.M_{KOH}.M_{FA}}{10.m_s} \quad (1)$$

where FFA (wt%) denotes the free fatty acids content (the weight percentage of free fatty acids in solution), V is KOH solution volume (mL) employed in the titration, M_{KOH} is the molarity of KOH solution (mol/L), M_{FA} is the average molar mass of fatty acids and m_s is the sample mass (g).

3. Results and discussion

The experimental results in terms of final acidity and process yield obtained from the alkaline washing tests are shown in Table 1 and for better visualization in Fig. 1. It should be emphasized that the test conditions do not reflect an attempt to perform an experimental design; instead, very scarce literature information, large-scale economical reasons (energy and material costs, separation feasibility) and industrial environmental experiences guided the tests.

As can be seen in this figure, for the crude biodiesel with initial acidity of 3.94 wt%, most of the experimental conditions led to FFA reduction below the upper limit value (0.25 wt%) specified by ANP and ASTM [9,10]. In fact, assays 2, 3, 5 and 7 to 11 provided acidity values “on spec” using milder reaction temperatures (35, 45 and 55 °C) and, in contrast to the traditional water and acid washing, a smaller amount of water, 2–3 wt% in relation to crude biodiesel, was required to achieve good FFA reductions and in some cases with minimum product losses.

These results are much better than that reported by Chongkhong et al. (2009) [14], where authors performed neutralization of crude biodiesel with initial FFA content of 1.4 wt% using 12 wt% NaOH solution (3 M) at 80 °C, reaching a final acidity of 0.33 wt%.

As can be seen from assay 13, in comparison with assays 12 and 14, the use of methanol showed to be necessary to help reducing product losses while keeping almost the same final acidity,

Table 1
Experimental conditions employed and results of alkaline washing of crude enzymatic biodiesel with initial FFA content of 3.94 wt%.

Assay	T (°C)	MeOH (wt%)	NaOH:FFA (eqv[a])	NaOH solution (wt%)	Final FFA content (wt%)	Yield (%)
1	35	1	0.5	3	1.07	96.6
2	35	1	1.0	3	0.19	96.2
3	35	1	1.3	3	0.21	96.7
4	45	1	1	1.5	0.93	89.4
5	45	1	1	2	0.23	85.6
6	45	1	1	2.5	0.32	86.2
7	45	3	1	2.5	0.23	80.8
8	55	1	1	1.5	0.14	84.2
9	55	1	1	2	0.12	80.5
10	55	1	1	2.5	0.19	83.1
11	55	3	1	2.5	0.23	80.3
12	65	1	1	1.5	0.70	10.0
13	65	0	1	1.5	0.98	91.0
14	65	1	1	1.5	0.71	10.0

[a] eqv - “equivalent”, stoichiometric relation between base and acid; T - temperature; MeOH - methanol.

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