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Biodiesel production by two-stage transesterification with ethanol

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A two-stage process consisting of two reactions steps with glycerin separation and ethanol/catalyst addition in each of them was optimized for ethyl esters production. The optimal reaction temperature was 55 °C. At an ethanol/oil molar ratio of 4.25:1 (25% v/v alcohol with respect to oil), a 99% conversion value was obtained with low ethanol consumption. In contrast to methoxide catalysts, sodium and potassium hydroxide catalysts severely complicate the purification since no phase separation took place under most conditions. With a total sodium methoxide concentration of 1.06 g catalyst/100 g oil, and adding 50% of the catalyst in each reaction step, biodiesel with a total glycerin content of 0.172% was obtained. The optimal conditions found in this study make it possible to use the same industrial facility to produce either methyl or ethyl esters.

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1. Introduction

Biodiesel is defined as a mixture of alkyl esters obtained by transesterification of vegetable oils or animal fats with a short-chain alcohol, typically methanol or ethanol. Ethyl esters-based biodiesel presents numerous advantages over more commonly used methyl esters. Ethyl esters exhibit lower particulate matter and green-house gases emissions, such as carbon dioxide and nitrogen oxides (NO_x), and are more biodegradable in water than methyl esters (Boehman, 2005; Makareviciene and Janulis, 2003). They present a higher cetane index and heating power (Clark et al., 1984) and lower cloud, cold filter plugging, and pour points (Encinar et al., 2007). Ethanol is generally obtained from agricultural sources and thus ethyl esters are a renewable biofuel. From an economical point of view, there is another important advantage of ethyl ester, which is related to the reaction stoichiometry (Scheme 1).

When the process yield is defined as the ethyl ester/triglyceride mass ratio, the maximum yield is 105.2% (ton of biodiesel/ton of oil) for ethanol, as compared to 100.5% for methanol. In the case of a production plant with a 300,000 ton/year capacity, for instance, this increase in yield represents and extra production of 12,000 ton/year, as compared to the production with methanol.

The technological and environmental advantages of ethyl esters, as well as the potential economical benefits, make their production process an interesting area of research. Ethyl esters can be obtained from vegetable oils and animal fats by alkaline (Alamu et al., 2008), acid (Morin et al., 2007), enzymatic (Moreira et al., 2007), or heterogeneously (Kim et al., 2010; Li et al., 2009) catalyzed reactions, and by non-catalyzed processes under sub or supercritical conditions (Warabi et al., 2004). However, alkaline catalysis is the most effective and widely used method (Meneghetti et al., 2006). Although transesterification with ethanol has been studied repeatedly (Bouaid et al., 2009; Černoch et al., 2010; Encinar et al., 2007; Marjanovic et al., 2010; Zhou et al., 2003), procedures that allow ethanol-based biodiesel production with high conversion levels under conditions suitable for industrial application have not been developed. Ethanol-based transesterification is extremely sensitive to minor changes in water content, reaction temperature, oil/ethanol ratio, and catalyst concentration; that can lead to a system with one or two phases at the end of the reaction. Determining accurate yields of ethanol-based biodiesel production is complicated by the fact that GC methods as described in the UNE-EN 14105 (2003) can be error-prone due to peak overlapping when monoglycerides are present. Therefore, in the current study, total glycerin content was analyzed by a volumetric procedure (Pisarello et al., 2010) which has no limitations regarding the raw material or the alcohol used in the reaction. For total ester content determination carried out according to the EN 14103 standard using the C17 methyl ester as internal standard, the response factor of ethyl esters must be corrected. These issues could account for the differences in ethyl ester yields reported by Soares et al. (2010), Bouiard et al. (2009), Encinar et al. (2007), and Issariyakul et al. (2008).

Obtaining economically acceptable transesterification is more difficult to achieve with ethanol than with methanol since glycerin and ethyl esters in the presence of ethanol are mutually soluble, which severely complicates phase separation after the reaction. Depending upon the ethanol/oil volume ratio fed to the reactor, phase separation may not occur spontaneously and necessitates the addition of glycerin (Encinar et al., 2007; Issariyakul et al., 2008) or evaporation of the ethanol (Bouaid et al., 2009). More

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$$\begin{array}{ccccccc} \text{Triglyceride} & + & \text{3 Ethanol} & \longrightarrow & \text{3 Ethyl ester} & + & \text{Glycerin} \\ \text{881 g/mol} & & \text{138 g/mol} & & \text{927 g/mol} & & \text{92 g/mol} \end{array}$$

Scheme 1. Ethanolysis reaction stoichiometry.

soap is formed in the presence of ethanol than methanol (Mendow et al., 2011) and the resulting stable emulsions complicate phase separation and necessitates washing procedure with large volumes of water (Encinar et al., 2007).

Mendow et al. (2011) studied single-step sunflower oil transesterification with ethanol in the presence of different catalysts and under various conditions, but were unable to attain biodiesel conforming to the international standards of 0.23 wt% bound glycerin. This outcome was mainly attributed to a very fast saponification, which consumes the catalyst.

In the current study a two-stage process, consisting of two reactions steps with glycerin separation and ethanol/catalyst addition in each of them was optimized for the production of ethyl esters, was implemented to increase the reaction conversion and thus achieve values required by the EN 14214 standard. Several catalysts and reaction conditions were used with the aim of optimizing the production process.

2. Experimental

2.1. Biodiesel production process

2.1.1. Transesterification reaction and phase separation

The reaction was carried out in a 0.5 L flask, with magnetic stirring, using a 50 mm teflon-coated magnetic bar, and a stirring speed of 1200 rpm. Refined sunflower oil (acidity <0.1 g oleic acid/100 g oil) was used as raw material to study the effect of different operation variables on the conversion. The effect of the temperature was studied using the refined sunflower oil and refined beef tallow (acidity <0.1 g oleic acid/100 g oil). Table 1 shows the fatty acid composition of the sunflower oil.

The reaction was carried out in two stages. The reaction temperature was varied between 45 and 70 °C, and reaction times from 30 to 120 minutes were tested. For the first stage, the oil was loaded into the reactor, and the temperature adjusted to the desired value. Once the oil reached this value, the alcohol containing the catalyst was added within a time range of 3 to 5 seconds. Time zero for the soap and catalyst measurements was the moment at which the ethanol/catalyst mixture was transferred to the reaction vessel.

Ethanol 99.5% purity (water content 1150 ppm) from Cicarelli was used as transesterification alcohol. Typically, the ethanol/oil molar ratios employed were 2.55:1 for the first stage and 1.7:1 in the second stage. On a volumetric basis, these ratios correspond to 15% and 10% v/v (volume of ethanol/volume of oil × 100), respectively. Experiments employing 30%, 40% and 50% v/v of ethanol were also carried out to study the effect of the ethanol content on conversion. The catalyst was either sodium or potassium hydroxide dissolved in methanol or ethanol, or sodium or potassium methoxide solutions (30 and 32 wt.% in methanol respectively) provided by Evonik-Degussa. The amount of catalyst was calculated such that it could neutralize the free fatty acids and catalyze the reaction. The catalyst concentration was varied between 1 and 1.44 wt.% (g catalyst/100 g oil).

Table 1
Fatty acid composition of refined sunflower oil.

Fatty acid	Composition wt.%
14:0	0.09
16:0	5.98
16:1	0.17
18:0	3.15
18:1	28.49
18:2	58.13
18:3	0.19
20:0	0.26
20:1	0.30
22:0	1.24

At the end of the first reaction step, phase separation was carried out in a separatory funnel at room temperature, the biodiesel-rich phase, which also contained the remaining ethanol, dissolved glycerin, and catalyst, was transferred to a 0.5 L flask, and the second reaction step was performed using the same procedure as the one employed during the first reaction step. The glycerin-rich phase formed during the second stage was separated using a separatory funnel.

The experiments were repeated once and the results for the two experiments differed by less than 11%.

2.1.2. Biodiesel purification

The biodiesel-rich phase was extracted with an aqueous solution of HCl 5 wt.% followed by extraction with water. Both extraction stages (washings) were carried out with gentle agitation at 60 °C, during 15 min. The volume of aqueous phase was 30% v/v relative to the biodiesel phase. The biodiesel was dried by stripping with nitrogen at 80 °C.

2.1.3. Effect of reaction temperature

A set of experiments was carried out to determine the effect of the reaction temperature. The total glycerin analyses were performed by gaseous chromatography, and also using the volumetric technique above mentioned. The total glycerin content is the sum of the bound glycerin (as mono-, di- and tri-glycerides) and the free glycerin. In this work, the biodiesel purification techniques employed were optimized in order to assure negligible free glycerin content in the final product. For this reason, the total glycerin content measured is the same as the bound glycerin, representing the percentage of non-converted glycerides. The total glycerin (T.G.) value is calculated with the following equation, from EN 14105:

$$\%\text{T.G.} = \%\text{G}_\text{F} + 0.255 \times (\%\text{M.G.}) + 0.146 \times (\%\text{D.G.}) + 0.103 \times (\%\text{T.G.})$$

Where %T.G. is the total glycerin percentage, $\%\text{G}_\text{F}$ is the free glycerin percentage, and %M.G., %D.G. and %T.G. are the monoglycerides, diglycerides and triglycerides percentages, respectively, obtained by gaseous chromatography.

The reaction temperature was varied between 45 and 65 °C. The raw materials evaluated were refined sunflower oil and refined beef tallow. The stirring speed was 1200 rpm, while the ethanol/oil molar ratio was 4.25:1 in all the experiments. The total catalyst concentration (sodium methoxide) used was 1.13 wt.% for the sunflower oil and 1.07 wt.% for the beef tallow.

2.1.4. Effect of the ethanol/oil ratio

The experiments were performed in two stages, using refined sunflower oil, 70 °C temperature, total catalyst concentration 1.06 wt.%., reaction time 30 and 60 minutes in the first and second stage, respectively, and stirring speed 1200 rpm. The ethanol used in the first and in the second reactions stages were (in a volumetric basis): 15%/10%; 15%/15%, 20%/20%, and 25%/25%, in the experiments carried out using a total amount of ethanol of 25%, 30%, 40%, and 50% v/v, respectively. These values correspond to a volumetric basis (volume of ethanol/volume of oil × 100). The ethanol/

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