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The Production of Biodiesel from Blended Commercial Oil in Mexico: A Comparative Study

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Abstract. Recently, a renewed interest has emerged in reformulated and alternative fuels as a way to control emissions and provide energy independence. Biodiesels (fatty acid methyl esters) derived from the transesterification of vegetable oils or animal fats with methanol are potential substitutes for petroleum-based diesel fuels. Compared with conventional diesel, biodiesel has the advantages of being biodegradable, renewable, non-toxic, and producing low emission of pollutants emissions (especially SO_x). The biodiesel yield and its ester content were dependent on the type of vegetable oil used; both of these parameters decrease when the vegetable oil´s acid value increased due to neutralization of the free fatty acids in the oil. The work that we present here describes a process for the preparation of biodiesel using blended commercial oils and lithium hydroxide as a catalyst. The viscosity, peroxide and acid value of biodiesel complied with specifications established by the EU (European Union) for this type of fuel.
Keywords: Biodisel, commercial oil, fatty acids.

Resumen. En la actualidad existe gran interés en reformular los combustibles, como una alternativa para controlar las emisiones y satisfacer las demandas energéticas. El biodiesel se obtiene por transesterificación de aceites vegetales o grasas animales con metanol y son los substitutos potenciales para diesel derivado del petróleo. Comparado con diesel convencional, el biodiesel tiene las ventajas de ser biodegradable, renovable, no tóxico, y generar emisiones bajas de contaminantes (especialmente SO_x). El rendimiento de Biodiesel y contenido de éster dependen del tipo de aceite vegetal, ambos disminuyen cuando el número ácido del aceite vegetal aumenta debido a la neutralización del contenido libre de ácido graso en el aceite. La presente investigación se enfoca en la obtención de biodiesel a partir de mezclas comerciales de aceite comestible e hidróxido de litio como catalizador. La viscosidad, el valor del peróxido, y el número ácido estuvieron dentro de las especificaciones de la comunidad europea establecidas para el biodiesel.
Palabras clave: Biodisel, aceite comestible, ácidos grasos.

Introduction

In the EU Directive 2003/30/EC, biodiesel is defined as a methyl ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel [1]. Biodiesel is a renewable, biodegradable alternative to petroleum diesel. Biodiesel, a product of vegetable oil and/or animal fat transesterification, is considered to be one of the most promising diesel fuel substitutes [2].

The research and development of biodiesel in México is in the early stages. The future economic development of our economic could be at risk, because of possible short term petroleum shortages and increasing concerns about environmental protection. So now it has become urgent to search for environmentally friendly fuels to begin substituting the diminishing petroleum reserves in México. Biodiesel is a typical kind of "green energy" that has a strategic significance for sustainable development.

Biofuels are an ideal alternative to dwindling fossil resources. In preparation for a future petroleum fuel crisis, the United States recently made a commitment to triple bioenergy usage within 10 years. The European Union also has made a similar proposal to ensure that biofuels account for at least 2% of the petroleum –based fuels market by the end of 2005 and a minimum of 5.75% of the market by the end of 2010 [3,4]. In recent years, several plants for the production of biodiesel have been installed in México.

The use of biofuels based on renewable resources has several advantages [5]. The advantages of the biofuels can be listed as follows: they reduce greenhouse gas emissions, they help to reduce the country's reliance on crude oil imports and supports agriculture by providing a new market for domestic crops; it enhances the lubricating properties; and it is widely accepted by vehicle manufacturers [6-8].

Although a wide variety of vegetable oils or their blends can be used to replace normal fuel, the high viscosities of the crude vegetable oils themselves limit their application. The solution of this problem involves transesterification of the triglycerides, with a short chain in the alcohol, such as methanol or ethanol, leading to less viscous methyl esters (FAMES) or ethyl esters (FAEES) respectively [4].

Biodiesel is an oxygenated fuel that is produced by transesterifying triglycerides from animal fats or vegetable oils with alcohol in presence of a homogeneous or heterogeneous catalyst. Any source of complex fatty acids can be used to produce biodiesel and glycerin [9-13].

In this study, blended food-grade oils, which are composed primarily of oleic and linoleic acids were chosen as the raw material for biodiesel production.

Experimental

Materials

The blended oils were food-grade and purchased from a local supermarket. Anhydrous methanol, lithium hydroxide, calcium chloride were reagent grade.

Analytical Methods

Biodiesel yield, relative to the amount of vegetable oil poured into the reactor, was calculated from methyl ester and vegetable oil weight. In addition, the vegetable oil, together with the methyl ester and glycerol layers were analyzed to calculate the material balance of the reactions. The material balance which refers to the initial amount of vegetable oil includes the molar yield of biodiesel and the molar yield losses due to triglyceride saponification and methyl ester in the glycerol phase.

The ester content means the methyl ester concentration (%wt) in biodiesel, and it was calculated by gas chromatography using a varian 3400CX instrument equipped with a capillary injection system operating at 240 ºC, with a split ratio of 100:1, and a sample size of 1μL. A capillary apolar column with 2.2 m in length, 0.32 mm of internal diameter, and 0.1 mm film thickness, was employed, and the column temperature program was: 50 ºC, initial temperature (1 min), 15 ºC/min to 180 ºC, 7 ºC/min to 230 ºC, and 30 ºC/min to 245 ºC. The detection system was equipped with a flame ionization detector (FID) operating at 250 ºC. The carrier gas was high-purity hydrogen.

The evaluation of oxidation stability, the iodine value, the peroxide value, the acid value, and the viscosity at 40 ºC, were determined after the biodiesel purification step. The iodine, acid, and peroxide values of biodiesel were calculated according to AOCS official methods [14], and the biodiesel viscosity was determined according to the EN ISO 3104 method.

General Procedure for Biodiesel production

The reaction of transesterification was carried out in a 1000 mL reactor, equipped with a thermostat, a mechanical stirrer, and condensation system. 1000 g of commercial oil was preheated to 65ºC for two hours at 600 rpm, then the methanol and lithium hydroxide (catalyst) were added. The catalyst at a concentration of 1.5 %wt of vegetable oil and a methanol-to-oil stoichiometric ratio (3:1) was used to obtain high conversion of oil into esters. The reaction was carried out at 65 ºC and atmospheric pressure for 30 min at 600 rpm.

After cooling, two phases were formed. The upper phase consisted of methyl esters, and the lower phase contained glycerol, the remaining catalyst together with the soaps formed during the reaction, and some entrained methyl esters and partial glycerides. After separation of the two layers by sedimentation, the crude ester was washed with distilled water (to remove the catalyst) until the pH of water used was lower than 7. The insoluble matter present in the methyl ester phase was eliminated with $CaCl_2$ followed by filtration. Finally, the biodiesel was refined by distillation at reduced pressure (less than 5000 Pa) and high temperature (higher than 250 ºC), until about 80% of the original volume of the biodiesel was obtained. The methods described here were previously reported [14-16].

Statistical Analysis

All the experiments were performed at least three times to determine the variability of the results and to assess the experimental errors. Arithmetical averages and the standard deviations were calculated for all the data. The following section shows the arithmetical averages of three experiments. In every case the corresponding standard deviations was low, and therefore the variability among the repeated experiments was insignificant.

Results and Discussion

The neutralization of the free fatty acids in the oil with lithium hydroxide produces soaps that dissolve in glycerol and, therefore yield reduction. Table 1 shows the oil characteristics, the material balance process and the methyl esters weights yields.

According to the results, it is possible to obtain nearly a 100% methyl ester yields from refined oils, but the ester yield may decrease when the vegetable oil´s acid value increases (Table 1). Furthermore, the ester and soap yield values indicated that, apart from the free fatty acid neutralization, some yield losses hat not been accounted for. On the other hand, the Table 1 presents the data of fat-oils composition, only with informative character.

The alcoholysis of vegetable oils is a three-step reversible reaction, where diglycerides and monoglycerides are intermediate products. In this case, we used refined vegetable oils and we did not observe dissolution of methyl ester in the glycerol, although we did not measure the mono- and diglycerides values. According to the biodiesel standard EN 14214, the monoglyceride content should be lower than 0.8 %wt and the diglyceride and triglyceride contents each lower than 0.2 %wt. In addition, the ester content should be higher than 96.5 %wt. In this study Oleico (safflower), crystal (sunflower), 123 (sunflower), Wesson2 (corn) did not meet the 96.5 %wt ester content, also these group of oils exhibited the highest glycerol weight yield (%), 3.97, 6.81, 4.0, 3.0, respectively.

Fröhlich *et al*. [17] found that the yield loss in the methanolysis of crude vegetable oil was also due to dissolution of the methyl ester in the glycerol and saponification of the triglyceride from the methyl ester soap. As shown in Table 2, the dissolution of methyl ester in the glycerol increased linearly with the free fatty acid level in the vegetable oil, however, the triglyceride hydrolysis increased just slightly with the free fatty acid content. All of the vegetable oils tested followed the same behavior, and the yield reductions are consequently independent of the triglyceride composition of the oil.

Figure 1 shows the iodine, peroxide, acid values, and viscosity for the chosen methyl esters.

Oxidation stability of biodiesel is related to its iodine value, which, in turn, is a measure of the unsaturation level. The specified limit for this parameter is 120 according to the biodiesel standard EN 14214. We found that the biodiesel obtained from

Table 1. Oil characteristics and methyl ester weight yields.

Oil commercial name (composition)	Sat fat (%wt)	Monosat fat (%wt)	Polysat fat (%wt)	Biodiesel yield (%wt)	Biodiesel acid value (mgKOH/g)	Glycerol weight yield (%wt)	Soap weight yield (%wt)
Oleico (safflower)	7.1	77.9	15.0	96.01	0.468	3.97	0.02
Wesson1 (canola)	10.7	64.3	25.0	97.59	0.201	2.0	0.41
Mazola1 (corn and canola)	14.3	57.1	28.6	96.5	0.141	3.0	0.5
Capullo (canola)	7.0	61.0	32.0	98.2	0.148	1.72	0.08
Crystal (sunflower)	9.3	54.3	36.4	93.1	0.439	6.81	0.09
123 (sunflower)	8.6	39.3	52.1	95.7	0.179	4.0	0.3
Wesson2 (corn)	17.9	25.0	57.1	96.4	0.041	3.0	0.6
Mazola2 (corn)	14.3	28.6	57.1	96.8	0.160	3.18	0.02
Maceite (corn)	12.2	30.3	57.5	96.8	0.093	2.95	0.25
Cocinera (corn, cotton, sunflower, safflower, canola, coconut)	14.3	25.0	60.1	97.89	0.11	2.1	0.01
Sarita (corn, cotton, sunflower, safflower, canola, coconut)	14.3	25.0	60.7	98.31	0.062	1.6	0.09

Table 2. Material balance of the process.

Oil commercial name (composition)	Vegetable oil free fatty acid content (%)	Biodiesel yield (% molar)	Triglyceride saponification (% molar)	Methyl ester in glycerol (% molar)	Total loss (% molar)
Oleico (safflower)	1.88	97.50	1.10	0.20	1.30
Wesson1 (canola)	0.59	96.4	1.85	2.76	4.61
Mazola1 (corn and canola)	0.50	97.42	1.12	0.44	1.56
Capullo (canola)	0.35	97.46	1.10	0.44	1.54
Crystal (sunflower)	2.91	95.95	1.2	3.5	4.7
123 (sunflower)	0.35	97.46	1.10	0.44	1.54
Wesson2 (corn)	0.02	97.90	0.9	0.49	1.39
Mazola2 (corn)	0.03	97.90	0.78	0.33	1.11
Maceite (corn)	0.025	98.1	0.8	0.4	1.2
Cocinera (corn, cotton, sunflower, safflower, canola, coconut)	6.47	89.99	1.77	9	10.77
Sarita (corn, cotton, sunflower, safflower, canola, coconut)	5.12	86.90	1.74	8.75	10.49

sunflower and safflower oils did not meet this specification because of their high content of unsaturated fatty acid chains. Deterioration of the methyl esters can be better determined if their peroxide, acid, and viscosity values are known.

Regarding the acid value, our numbers were low and within the EU specifications (> 0.5 mg KOH/g). Thus, the level of fatty acid remains stable, which means that hydrolysis of methyl esters to fatty acids, was not significant.

The viscosities of the methyl esters analyzed were within specifications (3.5-5 mm^2/s). In this regard, it seems that the initially formed hydroperoxides did not produce oxidized hydrocarbons and polymers. Previous work has shown that these secondary oxidations products increase the viscosity of the methyl esters produced. Nonetheless, to avoid further oxidation, special precautions must be taken during the storage of biodiesel produced from these blended oils.

Conclusions

The principal objective of this study was to demonstrate that biodiesel can be produced from blended oils, independently of their composition, source, and degree of fat saturation.

The best results were obtained with canola oils, and blended oils. Lithium hydroxide and methanol can be successfully used to catalyze the transesterification reaction.

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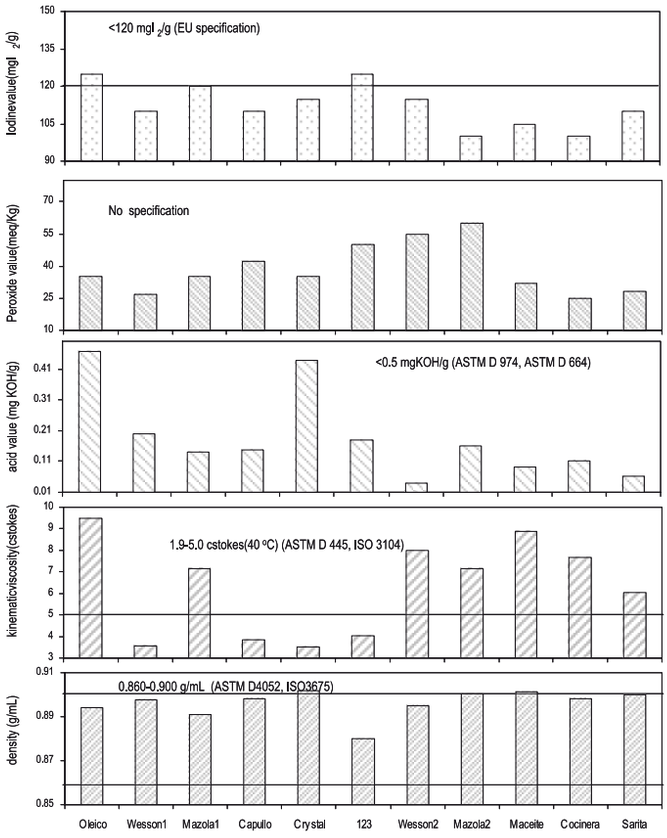

Fig. 1. Properties of Biodiesel produced.

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