



Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: Optimization of fuel properties



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ABSTRACT

The present work studies the influence of waste fish oil, palm oil and waste frying oil as raw material on biodiesel properties. The experimental planning was executed through acid esterification (6:1 methanol to oil ratio, 1 wt.% sulfuric acid, at 60 °C, 1 h) followed by transesterification (9:1 methanol to oil ratio, 0.5 wt.% sodium hydroxide, at 60 °C for 1 h). Biodiesel samples showed yield higher than 82%, reaching 90% for palm oil (33.3 wt.%) and waste frying oil (66.7 wt.%) biodiesel. FAME content was higher than 92.3% and had a maximum of 98.5% for waste fish oil (33.3 wt.%) and palm oil (66.7 wt.%) biodiesel. Special cubic models were used to fit experimental data, and were optimized by response surface methodology and multi-objective optimization. Viscosity (4.3 mm²/s) and COM (2.5 °C) were minimized when pure fish oil was used as raw material, whereas IP maximum (22.0 h) was found for palm oil biodiesel. Multi-objective optimization evidenced that although the use of the pure oils as feedstock presented more advantages to biodiesel properties, the waste fish oil (42.1 wt.%) and waste frying oil (57.9 wt.%) mix is beneficial, if the aim is IP (20%) and COM (80%) improvement.

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1. Introduction

Biodiesel is defined as mono-alkyl esters of vegetable oils or animal fats, obtained by transesterification of an oil or fat with an alcohol [1]. It is a biodegradable and nontoxic biofuel, so is environmental beneficial [2]. That is one of the reasons why biodiesel has received increasing attention, besides the fact of petroleum reserves are diminishing and it is necessary to find other competitive energy sources [3].

Fish oil is recommended in a healthy diet because of its content in omega-3 polyunsaturated fatty acids such as eicosapentaenoic (EPA) and docosahexaenoic (DHA) acids. [4]. However, refining of fish oil extracted from fish wastes would result in low yields because of its high content of free fatty acids and oxidation products [5]. Moreover, waste fish oil might have a low amount of EPA and DHA reducing its application on the pharmaceutical and functional food fields [6]. Thus, biodiesel using waste fish oil as feedstock has been recently researched [7–12]. Nevertheless, biodiesel from fish oil has low oxidative stability, mostly due to its high content of polyunsaturated fatty acids (PUFA) containing more allylic methylene positions [13]. Biodiesel oxidation is undesirable because it can increase viscosity and may lead to formation of insoluble species, which can lead to clog fuel lines and pumps [14]. In order to improve this property, antioxidants can be added to biodiesel [15] or fish oil can be mixed with more stable oils and used as biodiesel feedstock [16].

In this sense, palm oil, which is usually employed as raw material for biodiesel production, has a high resistance to oxidation due to its significant content of saturated fatty acids (SFA) [17]. Hence, it can be an appropriated oil to be mixed with fish oil before transesterification. Furthermore, waste frying oil, which is also more oxidatively stable than fish oil, is a substantial alternative of feedstock since it is cheap and diminishes the environmental impacts of inappropriate waste oil disposals [18]. Most of the scientific works on oil mixtures as feedstock are devoted to vegetable oils such as rapeseed, soybean and sunflower [19,20]. Some studies are also focused on mixtures of vegetable oils and animal fats. For instance, Galvan et al. [21] evaluated the oxidative stability of biodiesel obtained from a ternary mixture of soybean oil (50%), beef tallow (20 wt.%) and poultry fat (30 wt.%). Nevertheless, except for the work of Costa et al. [16] who carried out a preliminary study on the production of biodiesel from a mixture of waste fish oil (20 wt.%) and waste olive oil (80 wt.%), studies evaluating the fuel properties of biodiesel obtained from mixtures of waste fish oil and vegetable oils have not been reported in the literature.

Therefore, the aims of this work were: a) to study, by means of experimental design and analysis of variance (ANOVA), the influence of mixtures of waste fish oil, palm oil and waste frying oil as feedstock on the fuel characteristics of the biodiesel obtained, b) to obtain, by means of response surface methodology, the feedstock mixture that optimizes viscosity, oxidative stability and cold flow properties of the biodiesel produced, and c) to determine, by means of multi-objective optimization, the feedstock mixture that optimizes simultaneously the fuel properties of the biodiesel samples.

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2. Materials and methods

2.1. Materials

Fish oil was purchased from Industrias Afines, S.L. (Pontevedra, Spain) and presented the following properties: acid value of 16.4 mg KOH/g oil, peroxide value of 2.5 meq O₂/kg oil and a composition of 32.7 wt.% in oleic acid, 11.7 wt.% in linoleic acid, 3.6 wt.% in EPA and 5.7 wt.% in DHA. Palm oil was donated by the company Lípidos Santiga S.A. (Barcelona, Spain) and presented an acid value of 16.3 mg KOH/g oil, peroxide value of 2.1 meq O₂/kg oil and a composition of 44.5 wt.% in palmitic acid and 38.6 wt.% in oleic acid. Waste frying oil was collected from local domestic consumers (Granada, Spain) and had an acid value of 2.4 mg KOH/g oil, peroxide value of 4.6 meq O₂/kg oil and a composition of 55 wt.% in oleic acid and 26.7 wt.% in linoleic acid. Sodium hydroxide (≥99%), potassium hydroxide in ethanol (0.1 M), n-heptane (≥99%) and methyl heptadecanoate (≥99%) were purchased from Sigma-Aldrich, while methanol (≥99.8%) and diethyl ether (≥99%) were acquired from Scharlau. Ethanol (≥99%) and anhydrous sodium sulfate (≥99%) were provided by Panreac, whereas sulfuric acid (95%) was purchased from VWR International. Phenolphthalein (1% in ethanol) was provided by J. T. Barker.

2.2. Production process

Waste fish oil, palm oil and waste frying oil were used to produce biodiesel. A simplex centroid design with 16 experiments was carried out. It comprised 16 different oil contents as biodiesel feedstock, including pure oils and mixtures of two and three oils in different ratios. The content in free fatty acids (FFA) of the three oils was higher than 2 mg KOH/g oil, what impairs the biodiesel production, since it reduces the yield because of soap formation. Therefore, a two-step process was performed [22]. The first step consists in an acid-catalyzed pre-treatment that converts the FFA content into methyl esters, reducing acid value below 2 mg KOH/g oil. In summary, 200 g of oil, methanol (molar ratio methanol to oil of 6:1) and 1 wt.% sulfuric acid as catalyst were placed into a flat-bottomed flask. The samples were stirred at 300 rpm and kept at 60 °C for 60 min, using a hot plate controlled by a thermo regulator. After the reaction ending, the reactor content was transferred to a separating funnel to settle for 1 h. The bottom phase containing mainly unconverted oil and methyl esters was collected to carry out the next step [13].

In the second step the unreacted oil was submitted to an alkaline transesterification. In brief, the collected phase from the first step was introduced into a flat-bottomed flask with methanol (molar ratio methanol to oil of 9:1) and 0.5 wt.% sodium hydroxide. The samples were also stirred at 300 rpm and kept at 60 °C for 60 min, using a hot plate controlled by a thermo regulator. It should be noted that some amount of the alkali catalyst may have reacted in the neutralization of the first step samples, which had an increased acidity.

After the reaction completion, the content of the reactor was poured into a separating funnel, where it settled during 1 h. Then, the top phase containing mainly methyl esters was collected to be purified by washing, three times, with distilled water at 50 °C [13]. The aim of this step is removing impurities, such as unreacted catalyst, soap, glycerol and unreacted methanol. Finally, samples were vacuum filtered through anhydrous sodium sulfate and stored under nitrogen in amber bottles at –20 °C until analysis.

2.3. FAME content and yield

Gas chromatography was used to determine the fatty acid methyl ester (FAME) content in biodiesel samples, using the European standard EN 14103 [23]. Samples were analyzed according to the method from Camacho-Paez et al. [24] in a gas chromatographer Agilent 7890A (Agilent Technologies, S.A., Santa Clara, California, USA) connected to a

capillary column of fused silica Omegawax (0:25 mm × 30 m, 0:25 μm standard film; Supelco, Bellefonte, PA) and a flame-ionization detector. Nitrogen was used as the carrier gas, and the total column flow was 44 ml/min. The oven temperature was initially set at 150 °C for 3 min, then increased at a rate of 10 °C/min until 240 °C, and then kept at this temperature during 12 min. Matreya (Pleasant GAP, PA) n-3 PUFAs standard (catalogue number 1177) was used for the qualitative fatty acid determination and methyl heptadecanoate was employed as analytical standard for the quantitative determination. Firstly, the FAME of biodiesel samples was identified and then the peak areas were utilized to quantify the FAME content, according to Eq. (1):

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100. \quad (1)$$

Where C = fatty acid methyl content (%); $\sum A$ = total peak area; A_{EI} = peak area corresponding to the methyl heptadecanoate; C_{EI} = concentration of methyl heptadecanoate solution in heptane (mg/ml); V_{EI} = volume of methyl heptadecanoate solution (ml); m = mass of biodiesel sample (mg).

The biodiesel yield was calculated following the Eq. (2):

$$\text{Yield} = \frac{M_{\text{Biodiesel}} \times C}{M_{\text{Oil}}} \times 100. \quad (2)$$

Where $M_{\text{Biodiesel}}$ = mass of final biodiesel (g); M_{Oil} = mass of oil used as raw material (g); C = fatty acid methyl content described above (%).

2.4. Kinematic viscosity

Oils and biodiesel viscosities were evaluated using a rotational viscometer Haake model VT500 and a NV sensor (Fisher Scientific, Aalst, Belgium). The samples were kept at 40 °C using a water bath and 10 ml of each sample was introduced between the two coaxial cylinders, maintaining the specified temperature. Shear stress (τ) was measured using different shear rates (γ), from 0 to 3000 s⁻¹. Then, the dynamic viscosity (μ , Pa.s) was determined by the slope of the line obtained when plotting shear stress (τ , Pa) versus shear rate (γ , s⁻¹) for all the samples. The density of all the samples was measured at 40 °C. Using an electronic pipette, 5 ml of each sample were taken and then weighted to determine its mass. The dynamic viscosity and density were used to determine the kinematic viscosity at 40 °C, expressed in mm²/s.

2.5. Oxidative stability

The biodiesel oxidative stability was evaluated using the Rancimat method, a test of accelerated oxidation. The Metrohm Rancimat model 743 (Metrohm Instruments, Herisau, Switzerland) apparatus was used to carry out the measurements as specified in the European standard EN 15751 [25]. A stream of filtered, cleaned and dried air in a rate of 10 l/h was bubbled into 7.5 g of biodiesel samples in a glass tube, maintained at 110 °C. The effluent air containing volatile organic compounds was bubbled into a vessel containing 60 ml of distilled water where the conductivity was continually measured. The induction period (IP) was automatically calculated by the program. It represents the resistance time (in hours) of the biodiesel to oxidation.

2.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was employed to evaluate the cold flow properties of the biodiesel produced. DSC heating curves were used to determine the completion of melt onset temperature (COM), minimal high melting peak temperature (P1) and melting

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