



## Optimization of biodiesel production from waste fish oil



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### ABSTRACT

The present study deals with the production of biodiesel using waste fish oil. The research assesses the effect of the transesterification parameters on the biodiesel yield and its properties, including temperature (40–60 °C), molar ratio methanol to oil (3:1–9:1) and reaction time (30–90 min). The experimental results were fitted to complete quadratic models and optimized by response surface methodology. All the biodiesel samples presented a FAME content higher than 93 wt.% with a maximum, 95.39 wt.%, at 60 °C, 9:1 of methanol to oil ratio and 90 min. On the other hand, a maximum biodiesel yield was found at the same methanol to oil ratio and reaction time conditions but at lower temperature, 40 °C, which reduced the saponification of triglycerides by the alkaline catalyst employed. Adequate values of kinematic viscosity (measured at 30 °C) were obtained, with a minimum of 6.30 mm<sup>2</sup>/s obtained at 60 °C, 5.15:1 of methanol to oil ratio and 55.52 min. However, the oxidative stability of the biodiesels produced must be further improved by adding antioxidants because low values of IP, below 2.22 h, were obtained. Finally, satisfactory values of completion of melt onset temperature, ranging from 3.31 °C to 3.83 °C, were measured.

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### 1. Introduction

The fish industry still generates large quantities of by-products, mainly because of fish processing and discards [1]. Although these wastes are generally employed to obtain low value products such as fish silage or fertilizer, highly valued commodities such as fish oil can be also produced from them [2,3]. Fish oil containing a high content of omega-3 PUFA (>20 wt.%) has gained an increasing interest in the pharmaceutical and functional food industries, due to the recognized health benefits of eicosapentaenoic (C20:5n-3) and docosahexaenoic acids (C22:6n-3) [4,5]. However, fish oil having a lower amount of EPA and DHA leads to very low yield of omega-3 concentrates which considerably reduces its applications on both fields [6]. In addition, fish oil extracted from fish wastes may not meet the quality criteria required for edible purposes [7].

In this framework, alternative uses for poor quality fish oil, for example as a fuel, need to be investigated. Although crude fish oil can be directly employed as combustible in boilers or furnaces, it may result in large particulate emissions and carbon deposits on

the fuel injectors [8]. As a solution, crude fish oil can be converted into biodiesel which is a renewable diesel fuel with a reduced viscosity and a low emissions profile [9]. Furthermore, using fish waste oil as feedstock for biodiesel has the potential to reduce the production costs drastically [10]. Biodiesel is a mixture of fatty acid alkyl esters mostly produced from the transesterification of fats and oils. In this process, the triglycerides contained in the oil react with an alcohol, commonly methanol, and a catalyst, usually sodium hydroxide (NaOH), to yield fatty acid methyl esters (FAME) [11]. This reaction is highly influenced by temperature, molar ratio of methanol to oil, reaction time, catalyst and free fatty acids content of the oil [12]. Although considerable research has been conducted on the optimization of biodiesel production from vegetable oils by this method, only a few studies have been carried out when employing fish oil as raw material.

In light of the above, the aims of this work were: a) to evaluate the influence of temperature, methanol to oil ratio and reaction time on the yield and fuel characteristics of biodiesel produced from crude fish oil via transesterification using NaOH with methanol, and b) to find, by using response surface methodology, the processing conditions which lead to optimum values for yield, kinematic viscosity, oxidative stability and cold flow properties of the biodiesel obtained.

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## 2. Materials and methods

### 2.1. Materials

The fish oil employed contained 90 wt.% of salmon oil and the remaining 10 wt.% as a mixture of other fish oil in season. It was purchased from Industrias Afines, S.L. (Vigo, Spain) and presented the following properties: acid value of 6.6 mg KOH/g oil, peroxide value of 6 meq O<sub>2</sub>/kg oil and a composition of 5.7 wt.% in EPA and 7.6 wt.% in DHA. Methanol ( $\geq 99.8\%$ ), sodium hydroxide ( $\geq 99\%$ ), sodium sulfate ( $\geq 99\%$ ), n-heptane ( $\geq 99\%$ ) and methyl heptadecanoate ( $\geq 99\%$ ) were purchased from Sigma–Aldrich, whereas sulfuric acid (95%) was provided by VWR International.

### 2.2. Production process

Due to the fact that the free fatty acids (FFA) content of the crude fish oil is higher than 2 mg KOH/g oil, which would negatively affect to the biodiesel yield because of soap formation, a two-step process was performed as suggested by El-Mashad et al. [7]. The first step consisted of an acid-catalyzed pre-treatment to esterify the FFA which permitted to reduce the acid value below 2 mg KOH/g oil before the alkaline transesterification. In brief, 200 g of salmon oil were introduced with methanol (molar ratio methanol to oil of 6:1) and 1 wt.% sulphuric acid as catalyst 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 completion of the reaction, the mixture was transferred to a separating funnel to settle for 1 h and the bottom layer containing the esterified fatty acids and the unconverted oil was separated.

In the second step, the unconverted fish oil from the first step was subjected to alkaline transesterification. In short, 200 g of oil were introduced with a given methanol amount and 1 wt.% sodium hydroxide as catalyst into a flat-bottomed flask. The samples were stirred at 300 rpm and kept at the selected temperature for a desired time. The three process parameters considered for this study were temperature, molar ratio methanol to oil and reaction time. A factorial experimental design comprising 27 runs was carried out, in which each input variable was set at three levels; 40, 50, 60 °C for temperature; 3:1, 6:1 and 9:1 for methanol to oil molar ratio; and 30, 60, 90 min for reaction time. After the reaction was completed, the content of the reactor was poured to a funnel to settle for 1 h. The alkyl esters were separated and purified by washing two times with distilled water at 50 °C to remove unreacted catalyst, free glycerol and the remaining methanol. Then, the methyl esters were vacuum filtered through sodium sulphate to eliminate residual moisture. The biodiesel samples were stored under nitrogen at 4 °C in amber bottles until analysis.

### 2.3. FAME content and yield

The FAME content of the biodiesel samples was determined according to the European standard EN 14103 [13] with some modifications. The methyl esters of biodiesel samples were analyzed according to the method described by Camacho-Paez et al. [14] with an Agilent 7890A gas chromatograph (Agilent Technologies, S.A., Santa Clara, California, USA) connected to a capillary column of fused silica Omegawax (0:25 mm  $\times$  30 m, 0:25  $\mu$ m 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 program was initially set at 150 °C for 3 min, then increased at a rate of 10 °C/min until 240 °C and maintained at this temperature for 12 min. Matreya (Pleasant Gap, PA) n-3 PUFAs standard (catalog number 1177) was used for the qualitative fatty acid determination and methyl

heptadecanoate was employed as internal standard for quantitative determination.

Once the FAME of the biodiesel samples were identified, the peak areas were employed to determine the FAME content of each sample by 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 ester content (%);  $\sum A$  = total peaks area;  $A_{EI}$  = area of the peak corresponding to 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 yield of the produced biodiesel was expressed as follows, Eq. (2):

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

where  $M_{\text{Biodiesel}}$  is the mass of purified methyl esters obtained,  $M_{\text{Oil}}$  is the mass of oil employed and  $C$  is the fatty acid methyl ester content determined as described above.

### 2.4. Determination of biodiesel characteristics

#### 2.4.1. Kinematic viscosity

Viscosity of the biodiesel samples were measured using a rotational viscometer Haake model VT500 and NV sensor system (Fisher Scientific, Aalst, Belgium). Each sample was placed between the two coaxial cylinders and set at 30 °C employing a water bath. Shear stress ( $\tau$ ) was measured at varying shear rates ( $\gamma$ ) from 0 to 3000 s<sup>-1</sup>. Then, the dynamic viscosity ( $\mu$ , Pa s) of each sample was determined as the slope of the straight line resulting when plotting shear stress ( $\tau$ , Pa) versus the shear rate ( $\gamma$ , s<sup>-1</sup>). Measurements were performed in duplicate.

The density determinations involve heating the biodiesel sample at 30 °C and then simply weighing the sample, at that specific temperature, to determine the mass of the sample with a known volume. Measurements were carried out in duplicate.

Once the dynamic viscosity and the density were measured, they were used to determine the kinematic viscosity at 30 °C for each sample. It was expressed in mm<sup>2</sup>/s.

#### 2.4.2. Oxidative stability

The Rancimat test was employed to determine the oxidative stability of the biodiesel samples according to the European standard EN 15751 [15]. A Metrohm Rancimat model 743 (Metrohm Instruments, Herisau, Switzerland) was utilized. A stream of filtered, cleaned and dried air at a rate of 10 L/h was bubbled into 7.5 g of biodiesel samples contained in reaction vessels. These vessels were placed in an electric heating block, which was set at 110 °C. Effluent air containing volatile organic acids from the oil samples were collected in a measuring vessel with 60 mL of distilled water. The conductivity of the water was continuously recorded and the induction period (IP) was automatically determined using the apparatus. The measurements were carried out in duplicate. Rancimat IP was expressed as resistance time (in hours) of the oil to oxidation.

#### 2.4.3. Differential scanning calorimetry

DSC curves are commonly employed to obtain information about the cold flow properties of biodiesel [16]. In this work, DSC heating curves were obtained for each biodiesel sample in order to determine their completion of melt onset temperature (COM).

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