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Biodiesel production from waste fish oil with high free fatty acid content from Moroccan fish-processing industries

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ABSTRACT

Moroccan waste fish oil was used as raw material to produce the biodiesel in this study. The biodiesel sample is achieved by a dual step esterification-transesterification acid-base to reduce the higher FFAs content of fish oil after a rapid method of purification. It is characterized by techniques such as Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR) spectroscopy, and the Gas Chromatography–Mass Spectrometry (GC/MS). The experimental results showed that biodiesel produced from waste fish oil contained a significantly greater amount of methyl ester group in the biodiesel sample. The GC/MS results showed the presence of a good quantity of palmitic acid, oleic acid and linolenic acid which are essential biodiesel components. The biodiesel did not contain any trace of glycerol and it did meet international standards.

1. Introduction

Nowadays, fishing is one of our most important industries which always try hard to increase the production of fisheries. Morocco is located in northwest Africa. It is bordered on the north by the Mediterranean Sea, on the south by Mauritania, on the east by Algeria and on the west by the Atlantic Ocean. Morocco is the first world producer of sardines called "Sardina pilchardus" and is also the second largest supplier of fish in Africa after Nigeria [1].

This wealth has led to an increased development of production, transformation and preservation of fish industries which generate large amounts of waste, A percentage of the total catch of fish is isolated as processing leftovers such as heads, fins, skin, frames, trimmings and viscera. More complete utilization is achieved by conversion of leftovers into fishmeal and fish oils. Indeed, the quantities of fish waste are estimated at several hundred thousand tons of waste per year [2], while experiments showed that fish oil recovered from fishmeal residue varies considerably between a mass fraction of 1.4% and 40.1% depending on the species, tissue and season [3]. Therefore, it would be useful to insist on the importance of treatment and recovery of fish waste to avoid any effect on the environment in general and on human health in particular.

In fact, many recent studies have been interested in the valorization of fish-waste. The one that has received the greatest attention is the synthesis of a biofuel that meets the security of supply criteria: response to local development needs ensuring the reduction of the production of CO_2, the main greenhouse gas emissions. Biofuel is an alternative fuel for diesel engines. It can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines [4–8].The biodiesel yield ranges between 80 and 95 wt% depending on the quality and the purity of the oil [9].

Research in this field is managed in order to improve the process of converting vegetable oil or animal fat into biodiesel. That is usually produced by different processes. Transesterification reaction is the most common method in the production of biodiesel. Some researchers indicated that the physical properties of biodiesel from fish waste oils, including viscosity and acidity, are much higher than regular diesel [9] which causes problems in performance and NO_x in the combustion of diesel engines [6,10]. It was noted that the acid value marked variation between different batches of fish (viscera, skin and muscle), and different type of fish [3]. Furthermore, it was found that due to the high acid value of salmon oil, alkaline-catalyzed transesterification was not an effective method for producing biodiesel from salmon oil [11],

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which indicates that the adopted process requires adjustment [8]. Moreover, other researchers showed that animal fat as well as vegetable oil have a higher heating value similar to that of the ordinary diesel, but the problem is their acidity which is superior to those of diesel [12]. The biodiesel produced from fish oil had a higher heating value compared to those of animal fat or vegetable oil [13]. It is also noted that the oil or fat used in the transesterification by basic catalysis should contain less than 0.5% free fatty acid (FFA) [14]. It has been known that, when the FFA level exceeds 0.5%, the soap formation occurs and inhibits the separation between the biodiesel and glycerol, and decreases the yield of the final product. Consequently, the direct transesterification by basic catalysis of this oil is not applicable. The pretreatment of this oil to remove the FFA and the water is usually required.

In this paper, acid catalyzed esterification and base catalyzed transesterification were used, respectively, to reduce the higher FFA content of waste fish oil and to produce biodiesel respectively. Initially, the esterification reaction was performed to investigate the effect of various reaction parameters on the reduction of free fatty acid content in waste fish oil. Methanol/oil ratio, catalyst amount, reaction temperature and time were optimized to determine the optimum conditions in the pretreatment step which gave the lowest acid value. Then, the second step, base catalyzed transesterification in which oil reacts with methanol in the presence of an alkaline catalyst (KOH) to form ester and glycerol, is performed.

2. Materials and methods

2.1. Materials

The feedstocks, Waste Fish Oil (WFO) sample, used in this study was supplied by Kilimanjaro Environment Company (Casablanca, Morocco) which is specialized in the collection of used vegetable and animal oils. It is recovered as waste from fish meal and oil plant operations. The chemicals were used without any prior purification: Sodium hydroxide (≥97%), potassium hydroxide (85–100%), diethyl ether (≥99.5%) and methyl heptadecanoate (≥99%) were purchased from Sigma-Aldrich, while methanol (≥99.9%), ethanol (≥99.9%) were supplied by Fluka, Hexane (95%), and cyclohexane (99.9%), and sulfuric acid (96%) were purchased from Panreac.

2.2. Methods

The physical and chemical properties such as viscosity, density, acid value of the reactants and the produced biodiesel were determined according to the ASTM standards. The obtained values were compared with the European standards of biodiesel [15]. To determine the fatty acid profile of waste fish oil and FAME produced in this work, a 2000 TR thermo gas chromatograph was used with a flame ionization detector (FID) and a capillary column DB-WAX (30 m × 0.32 mm, 0.23 μm film thickness). Helium was used as carrier gas. The temperature program started at 60 °C (for two min) and continued with a ramp of 6 °C/min to 150 °C (for 10 min), and then with a ramp of 10 °C/min to 250 °C (for 2 min). Infrared spectral data were collected by using a VERTEX 70 spectrometer equipped with ATR MIRACLE DIAMANT technique. The device had a spectral range of 4000–650 cm^{-1}.and spectral data were collected by co-adding 16 scans at a resolution of 4 cm^{-1}. The ^{1}H-NMR spectra were recorded at 298 K with a BRUKER AVANCE 300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent. ^{1}H-NMR spectra were recorded with pulse duration of 30°, a recycle delay of 1.0 s and 8 scans. The ^{13}C NMR (75 MHz) spectra were recorded with pulse duration of 30°, a recycle delay of 1.89 s and 160 scans. Nuclear Magnetic Resonance Spectroscopy can be used for the determination of the conversion of transesterification reaction in progress. The conversion is illustrated by the following equation as previously described [7,16].

$$C = 100x\frac{2A_{Me}}{3A_{CH2}} \quad (1)$$

where:

C = conversion of triacylglycerol feedstock to the corresponding methyl ester.

A_{Me} = integration value of the protons of the methyl esters (the strong singlet peak).

A_{CH2} = integration value of the methylene protons.

The factors 2 and 3 derive from the fact that the methylene carbon possesses two protons and the alcohol (methanol-derived) carbon has three attached protons.

2.3. Biodiesel production

2.3.1. Pretreatment of the waste fish oil

First, the oil was filtered under vacuum to remove any solid impurities and a portion of water. Then, it was degummed with phosphoric acid and water to remove polar component such as phospholipids, lecithins, pigments and some contaminant such as heavy metals. The neutralization was realized by the addition of potassium hydroxide to remove free fatty acids as soap. Silica gel column chromatography was then applied to remove remaining impurities and colorant using (90% cyclohexane and 10% Ethyl Acetate) as solvent. It was also dried simply by heating at 105 °C in 15 min. This time was determined by monitoring the weight loss upon heating. Finally, the deodorization was carried out by heating under vacuum. The intensity of the scent is followed by a simple flair, and it was weighed into a Pyrex tube then subjected to vacuum heating at 90 °C. Fig. 1 illustrates fish oil before and after purification.

2.3.2. Esterification-Transesterification process

Biodiesel production from WFO was performed by Esterifica tion-transesterification occurred out in two steps. First, the esterification reaction was performed in a three-neck round bottom flask (Ace Glass Inc.) equipped with a thermometer to measure the temperature, a water cooled condenser was connected to another neck

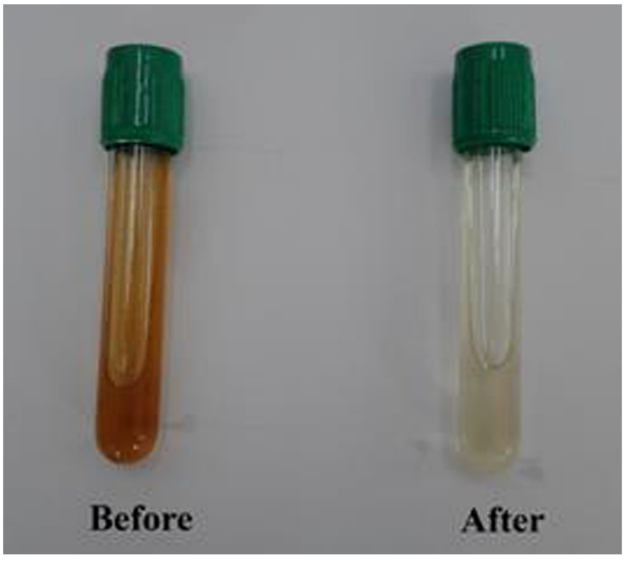

Fig. 1. Waste fish oil before and after purification.

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