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Biodiesel production using oil from fish canning industry wastes

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ABSTRACT

The present study evaluated biodiesel production using oil extracted from fish canning industry wastes, focusing on pre-treatment and reaction conditions. Experimental planning was conducted to evaluate the influence of acid catalyst concentration (1–3 wt.% H_2SO_4) in the esterification pre-treatment and the amount of methanolic solution (60–90 vol.%) used at the beginning of the further two-step alkali transesterification reaction. The use of a raw-material mixture, including waste oil obtained from olive oil bagasse, was also studied. The results from experimental planning showed that catalyst concentration mostly influenced product yield and quality, the best conditions being 1 wt.% catalyst and 60 vol.% of methanolic solution, to obtain a product yield of 73.9 wt.% and a product purity of 75.5 wt.%. Results from a one-step reaction under the selected conditions showed no advantage of performing a two-step alkali process. Although under the best conditions several of the biodiesel quality parameters were in agreement with standard specifications, a great variation was found in the biodiesel acid value, and oxidation stability and methyl ester content did not comply with biodiesel quality standards. Aiming to improve fuel quality, a mixture containing 80% waste olive oil and 20% of waste fish oil was evaluated. Using such mixture, biodiesel purity increased around 15%, being close to the standard requirements (96.5 wt.%), and the oxidation stability was in agreement with the biodiesel quality standard values ($\geqslant$6 h), which are promising results clearly showing the potential of using such wastes, of very low value, for biodiesel production.

1. Introduction

A biofuel is, in simple terms, a combustible material obtained from renewable biomass resources, commonly used as an alternative, cleaner fuel.

When properly produced, biodiesel can be used pure or in mixture in most current diesel vehicles, with minor adaptations. The quality requirements for this automotive diesel substitute can be found in standards. At present, the standard used in Europe for 100% fatty acid methyl esters (FAME) is the EN 14214:2008+A1:2009. In case of the produced biodiesel fail the standard requirements, due to raw material characteristics, it might be used in boilers for heat generation (depending on its characteristics); alternatively, raw materials might be mixed or the fuel blended with diesel to improve its quality [1].

Biodiesel production is generally made at a larger scale by a transesterification reaction, using selected feedstock, normally virgin vegetable oils [2]. However, their high prices and use as food resource (if edible) are limiting factors. Therefore, efforts have been made to find alternative raw materials.

The use of waste materials brings a valuable contribution, not only in the reduction of biodiesel production costs but also in the better waste management results, avoiding subsequent environmental impacts. Waste frying oils are deeply studied as alternative raw materials [3–7]. The impact of this responsible application, even though relevant, is limited, considering their availability. Industrial waste oils and fats are however more abundant. When compared with biodiesel from vegetable origin, biodiesel from fats has the advantages of a higher calorific value and cetane number, being however less stable to oxidation and presenting a higher cold filter plugging point [8].

For countries with a considerable expression of the fish canning industry there is the possibility to use oily fish discarded parts as feedstock for the biodiesel production. The use of such alternative raw material, that represents a challenging waste management problem for the industries, is, however, still understudied.

The oil extraction is performed mainly in marine oily fishes such as mackerel, salmon, tuna and codfish, which present a considerable oil content [9–13]. The usable parts, that can represent around 25 wt.% of the fish, are, in general, the viscera, head, fins, and tails, amongst others [12]. On the other hand, considering

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the 2006 Best Available Techniques in the Food, Drink and Milk Industries Reference Document (BREF) [14], the expected range for solid wastes generated during fish processing is 20–60% of the catch, comprising heads, viscera, skins and other parts.

Regarding Northern Portugal's sea canning industry, the oily fishes transformed are mainly sardine, mackerel and tuna. Considering the information gathered from contact with the existing plants (information given on a confidential basis), it can be estimated that more than 150 t of fish oil are produced annually and, also, that more than 40 t are, in addition, washed away by the wastewaters. Currently, the reported fish oil that is extracted is being, essentially, commercialized for incorporation in animal feed or processed for use as a soil supplement. The energetic potential of such waste is however not being used by the industries.

Table 1 presents the characteristics of the raw oil extracted from the discarded parts of various marine fishes. The elementary composition shows around 77 wt.% of carbon and 12 wt.% of hydrogen [15]. The most common fatty acids found in these fish oils, ordered by carbon chain increase, are: myristic (C14:0, up to 7 wt.%), palmitic (C16:0, up to 20 wt.%), palmitoleic (C16:1, up to 28 wt.%), stearic (C18:0, up to 7 wt.%), oleic (C18:1, up to 42 wt.%) and also significant amounts of polyunsaturated fatty acids (PUFA) such as arachidonic (C20:4, up to 3 wt.%), eicosapentaenoic (C20:5, up to 11 %), docosapentaenoic acid (C22:5, up to 15 %), and docosapentaenoic (C22:6, up to 39 wt.%) [9,10,12,16,17]. It should be noted that the PUFA are considered beneficial for feed purposes [18]; regarding biodiesel production, fluidity of the fuel is improved compared to other raw materials, which might be an advantage. On the other hand, the presence of PUFA might increase fuel instability since degradation tends to be accelerated in more unsaturated esters.

Biodiesel current production process includes several steps: raw material pre-treatment (if necessary) to remove impurities and undesirable characteristics, transesterification reaction, phase separation and product purification (usually washing and drying) [2].

Common feedstock characterization to evaluate pre-treatment needs includes water content and acid value determination. In particular, the reduction of the acid value is an important pre-treatment as the removal of the excessive amount of free fatty acids is vital, especially when using alkaline catalyzed transesterification. The idea is to prevent the formation of soaps and consequently avoid a poorer catalytic activity and emulsifying soap effects that reduce biodiesel yield and quality [1,19].

Biodiesel transesterification reaction occurs between the triglyceride source and a short-chain alcohol (mostly methanol) to produce a mixture of FAME and glycerol. The reaction might be catalyzed by enzymes, acid or alkaline homogenous catalysts [20] and heterogeneous catalysts [21]. The most commonly used are the homogeneous alkaline catalysts [2,20] due to low cost and high efficiency. NaOH, KOH and their methoxydes are the commonly used catalysts. Since it is a reversible reaction, an excess of alcohol (usually 6:1 methanol to oil molar ratio) is usually used to force the reaction towards the products.

When the fish oil presents high acidity, an acid esterification pre-treatment might be performed. In a study by El-Mashad et al. [10], an acid esterification using 1 wt.% H_2SO_4 and a reaction temperature around 52 °C, during 1 h, was performed (molar ratio methanol:oil of 6:1, 600 rpm stirring) to reduce the acid value of a salmon oil (3.5 or 12 mg KOH g^{-1}) to values acceptable for alkaline transesterification (considering a maximum of 2 mg KOH g^{-1}).

The fish oil biodiesel synthesis, that follows pre-treatment, is usually, but not exclusively, reported as single stage alkaline transesterification process (methanolic route). Few studies have been performed in biodiesel production from fish oil; however, according studies found [9–13], common conditions include: (i) NaOH (1 wt.%) or KOH (0.5 wt.%) as catalysts; (ii) 6:1 to 9:1 methanol to oil molar ratio; (iii) reaction temperature between 50 and 60 °C; (iv) reaction time between 30 and 60 min; and, (v) stirring from 600 to 6000 rpm. These are conditions conventionally used in most alkaline transesterification reactions [2].

After phase separation, methyl esters/biodiesel purification is usually performed. First, the methanol in excess is recovered by distillation, water washing is used to remove the homogeneous catalyst and drying is performed to remove residual water [10–13,16], as in general alkali transesterification processes.

Regarding the characterization of the obtained biodiesel, Table 2 reports data collected from the revised literature and compares it with the general applicable requirements according to the European Biodiesel Standard EN 14214. The studies show that biodiesel quality varies considerably and that it might be difficult to fulfill some of the required parameters. Therefore, further studies are required to evaluate and if possible improve biodiesel quality.

The biodiesel composition varies according to the fish oil characteristics and fatty acids found agree with the ones reported previously for oils. It should be, however, mentioned, that a greater range of values were found for the composition of FAME due to the great variability of fish oils and mixtures used as raw materials.

In order to improve product quality, pre-treatment conditions should be studied and optimized. In a study by Dias et al. [1], the catalyst concentration during the acid esterification pre-treatment of a waste fat was found to be a key parameter.

Table 1
Characteristics of fish oil extracted from marine wastes [10,15,16,20,25].

Parameter	Result
General characteristics	Dark brown, viscous liquid with a distinctive smell
Water content (wt.%)	0.05–0.26
Acid value (mg KOH g^{-1})	0.1–28.4
Iodine value (g I_2/100 g)	88[a]
Density (kg m^{-3})	875.3–978.9
Calorific value (MJ kg^{-1})	39.71–40.21
Flash point (°C)	156.0–178.5
Kinematic viscosity at 40 °C (mm^2 s^{-1})	3.883–4.360

[a] Wiggers et al., 2009.

Table 2
Quality parameters of biodiesel obtained from waste fish oil [9–13,16,17,20,27,28] and European Biodiesel Standard (EN 14214) requirements.

Parameter	Result	EN 14214
Aspect	Transparent yellow, but varies depending on the feedstock nature/condition and the processing	NA
Water content (mg kg^{-1})	619[a]	⩽500
Acid value (mg KOH g^{-1})	0.26–1.19	⩽0.50
Density (kg m^{-3})	860–889	860–900
Cetane number	50.9[b]	⩾51.0
Flash point (°C)	103–220	⩾101 °C
Kinematic viscosity at 40 °C (mm^2 s^{-1})	4.0–7.2	3.50–5.00
Methyl ester content (wt.%)	95.74–100.00	⩾96.5

NA – Not applicable.
[a] Fan et al., 2010.
[b] Lin and Li, 2009.