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Ethanolysis of fish oil via optimized protocol and purification by dry washing of crude ethyl esters

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ABSTRACT

In this research work, fatty acid ethyl ester (biodiesel) was successfully developed from fish oil. The acid value of fish oil used is 1.23 mg KOH/g. As a result, transesterification of fish oil with ethanol was performed via one-step transesterification, namely alkaline-catalyzed transesterification using potassium hydroxide (KOH) as a catalyst. The influence of transesterification variables including amount of KOH, ethanol to oil molar ratio, reaction temperature, reaction time and type of the alkali catalyst on yield of fish oil ethyl esters (FOEE) were investigated. The dry washing method which used the activated carbon produced from de-oiled fish waste was used to purify the crude ethyl esters. The best yield of FOEE (98.04% ~ 97.11% w/w ester content) was obtained at 0.75% wt. KOH, 9:1 ethanol to oil molar ratio, 70 °C reaction temperature and 60 min of reaction. The fuel properties of FOEE were complied with the limits prescribed in the ASTM D6751 standards and EN 14214, where applicable. The viscosity of the produced ethyl ester was found much lower than those reported for the ethyl esters produced from various feedstocks. The transesterification of fish oil with ethanol followed first order kinetics and the activation energy was found to be 14.45 kJ/mol.

1. Introduction

Biodiesel (BD) was used as a successful alternative to petro diesel due to its renewability, non-toxicity and bio-degradability. Moreover, no poisonous pollutants are emitted from it on combustion [1–3]. Production of BD from vegetable oils was widely investigated [4–8]. However, there are some restrictions on the use of vegetable oils in the production of BD, because lands available to cultivate various seed oils are limited. Furthermore, most of vegetable oils are important source of food for humankind. Thus, it is very important to find non-edible feedstocks for BD production.

Animal fats such as chicken, beef, duck and lard fats were widely used in the production of BD, because their availability are more guaranteed when compared to vegetable oils. Furthermore, most of animal fats are disposed as wastes. In addition, animal fats are not recommended for human as a source of food due to its negative impact on the health [9–15]. The BD produced from animal fats has higher oxidation stability and higher cetane number than vegetable oils due to their higher content of saturated fatty acids [1].

Iraq is a fish producer country and is one of the major fish producer countries in the world. Besides petroleum, Iraq is also rich in different types of fish found in Tigris and Euphrates rivers as well as Hawizah marsh. *Grypus Barbus, Barbus luteus Heckel, Hypophthalmichthys molitrix and Silurus triostegus Heckel* are the main types of fish that can be caught in fresh water surfaces in Iraq. Fish slaughter houses produce various fish wastes such as backbone, skin, fatty layers, heads, tail and stomach which are either disposed as waste or may be used as a manure. Due to the environmental and health risks associated with accumulation of such waste, it is either used as fertilizers or in the production of protein concentrates which in turn is used as feed for fish. Therefore, such waste represents a real threat to the environment unless it is handled. Recycling oil from this waste and using this raw material for BD production may be one of the real solutions [14,15].

Fatty acid ethyl ester (FAEE) emits less greenhouse gases (CO_2 and NO_X) as well as particulate matters than fatty acid methyl ester (FAME). Moreover, it is more biodegradable in water than FAME and has higher cetane number and heating value but lower cloud and pour points than FAME. However, production of FAEE through alkali-catalyzed transesterification is difficult compared to FAME due to the formation of stable emulsion during ethanolysis process which makes separation of glycerin from BD very hard [16].

Water washing method is widely used in the purification of BD after separation of glycerin. However, a part of the ester is lost in the form of soaps which happens more in the case of ethanol than methanol. Moreover, wet washing method produces large amounts of the contaminated water which contains various pollutants such as glycerin, soap, free fatty acids, methanol and oil. As a result, treatment of the wastewater is necessary and thereby, the cost of production

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increases. Consequently, the dry washing method using various adsorbents such as ion-exchanger, magnesol, activated carbon and rice husk ash was proposed to avoid loss of ester in the form of soaps. Furthermore, the use of adsorbents for purifying the crude BD reduces amounts of the polluted water originated during the production of BD [17–20]. Activated carbon has higher surface area and various pore size distribution which help in removing pollutants of various molecular sizes. Besides, the use of adsorbents in the purification of BD results in bleaching and de-coloring of the produced BD [20].

Few works were reviewed in the literature on the production of FAEE from animal fats [21,22]. The only published research on the production of FAEE from fish oil was used ultrasonic energy [23]. To the best of the author's knowledge, the optimized ethanolysis of fish oil with the purification of the crude ethyl esters through the dry washing method using the activated carbon produced from its de-oiled solid waste was not reported in the literature.

Herein, FAEE was produced from fish oil via KOH-catalyzed transesterification with ethanol. The crude ethyl ester was purified by using the activated carbon produced from de-oiled fish waste. Ethanolysis variables such as amount of KOH, ethanol to oil molar ratio, reaction temperature, reaction time and type of the alkali catalyst were investigated. Properties of the produced ethyl esters were evaluated in accordance to the ASTM standards. Kinetics of transesterification of fish oil with ethanol was also investigated, and finally different blends of FAEE and petro diesel were prepared and studied.

2. Experimental

2.1. Materials

Fish wastes were collected from the fish Slaughterhouse located in the city of Mosul, north of Iraq. Chemicals and solvents used in the present study were of analytical reagent grade and were used as received without any further purification. Absolute ethanol (99.90%), potassium and sodium hydroxides (KOH and NaOH, pellets), sodium methoxide (CH_3ONa), sodium ethoxide (CH_3CH_2ONa), potassium iodide, formic acid, sodium periodate and sodium sulfate (Na_2SO_4) were purchased from Merck (Darmstadt, Germany). Chloroform, *n*-hexane, phenolphthalein indicator, and hydrochloric acid were provided from Fluka (Swiss).

2.2. Extraction of fish oil

The fish oil was extracted from the discarded parts of fish (fatty layers, backbone, tails, heads and skin) without any chemical treatment as shown in Fig. 1. The fish waste was placed into a 1 L conical flask. The flask was then heated by a boiled water bath in order to melt the oil. The fish oil was then separated from the solid impurities such as meat and particles of bones by filtration. The obtained oil was then transferred to a separating funnel and left overnight to separate water (if any). The oil was dried over freshly activated sodium sulfate (Na_2SO_4), placed in a dark container and kept at 5 °C for further use. The yield of fish oil (FO) was calculated on weight basis.

2.3. Transesterification of fish oil with ethanol

Ethanolysis of FO was performed using a 500 mL round-bottom flask provided with thermostat, mechanical stirrer, sampling outlet, and a condenser. The FO (100 g) was fed to the reactor and then a freshly prepared ethanolic potassium hydroxide solution (a pre-established amount of KOH dissolved in ethanol at 6:1 ethanol to oil molar ratio) was added to the oil. The mixture was heated by using a digital water bath at 70 °C for 60 min with simultaneous stirring at 600 rpm. After completion of the reaction, the products were transferred to a separating funnel and left overnight to obtain two layers. After separating the glycerin (lower layer), excess ethanol was recovered from the ethyl esters layer by using a rotary evaporator [3,4]. The unpurified ethyl ester was mixed with the AC (3 wt.%) for purification. Finally, the ethyl esters yield was determined as follows [20,24].

$$\text{Product yield (wt.\%)} = \frac{\text{Weight of FOEE produced}}{\text{Weight of oil used}} \times 100$$

$$\text{Biodiesel yield (wt.\%)} = \frac{\text{Weight of purified FOEE}}{\text{Weight of oil used}} \times 100$$

2.4. Analysis of fish oil ethyl esters

The fatty acids composition of FOEE was analyzed using gas chromatography (GC, Perkin Elmer, Auto system GLX, Shelton, U.S.A.). A silica capillary column (Supelco SP™-2380, 30 m, 0.25 mm i.d., 0.25 μm film thickness) provided with a flame ionization detector (FID) was used for separation. The sample was dissolved in hexane and helium was used as the carrier gas at a flow rate of 0.5 mL/min. The injector and detector temperature were 280 and 260 °C, respectively.

The method proposed by Bindhu et al. [25] was used to determine the ester content on the BD samples. The thin layer chromatography (TLC) was used as a rapid and an easy means to monitor ethanolysis of fish oil by using silica gel plates and the iodine vapor to visualize the spots after fractionation [15]. The key functional groups on the BD and the parent oil were determined using the Fourier transform Infra-Red (FTIR) spectrum (Biotechnology, UK).

2.5. Testing and evaluation of fuel properties

Fish oil ethyl ester produced was evaluated for several interesting properties according to ASTM procedures. Density was measured at 15.6 °C according to ASTM D 4052-91 using a calibrated pycnometer. A kinematic viscometer (Canon F F24 U-tube glass viscometer) was used to determine viscosity of FOEE at 40 °C according to (ASTM D 455). The refractive index (D1747–09) was measured at 20 ± 0.1 °C using the Abbe refractometer connected to a thermostatically controlled water bath that maintained the temperature of the refractometer. The cloud point and pour points were determined according to ASTM D 2500. Conradson carbon residue (ASTM D4530) was used to determine the amount of carbon remained after complete burning of FOEE. The acid value (ASTM D664) was determined using titration method. The flash point (ASTM D93) was determined using a Pensky–Martens closed-cup tester. The iodine value (IV) was measured according to Hanus method. The cetane number was determined using a digital cetane number meter (Shatox, Russian Federation). The total glycerin of the produced fuel was determined using method proposed by Pisarello et al. [26]. The glycerin titration was based on its oxidation to formic acid using sodium periodate, followed by a titration with sodium hydroxide [26]. Soap content was determined in accordance with AOCS Cc 17-95.

2.6. Preparation of activated carbon from de-oiled fish waste

After extraction of the oil from fish waste, the de-oiled residue was used as a feedstock to produce the activated carbon (AC) via one-step process, *i.e.* carbonization and activation method as depicted in Fig. 1. The de-oiled waste was mixed with a solution of phosphoric acid (50% H_3PO_4 v/v) and left for a day. The mixture was then filtered and oven dried until all water was evaporated. The product was then activated in a muffle furnace at 600 °C for 1 h. The produced carbon was washed with (0.1 M solution of HCl) and then by distillated water until neutral water was obtained [27]. The carbon was then dried, crushed and allowed to pass through a (100 μm) sieve.

The micro pore surface area of the produced AC was determined using ethylene glycol mono ethyl ester (EGME) retention method

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