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Biodiesel production from mixed non-edible oils, castor seed oil and waste fish oil

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ABSTRACT

Biodiesel production from non-edible oils is one of the effective approach to reduce cost of production, and solve part of the obstacles facing the availability of the traditional raw materials. The present investigation explores biodiesel production from mixed non-edible oils, castor seed oil (CSO) and waste fish oil (WFO). Different blends of WFO and CSO (10:90–50:50% WFO:CSO w/w) were implemented and evaluated in order to select the optimal blend that possesses properties closer to those of conventional raw oils that were used for biodiesel production. The equivalent blend (50:50% WFO:CSO w/w) was found to be the optimal blend; thus, it was transesterified with methanol to produce fatty acid methyl ester. Effect of the operating and processing variables, such as the type and the concentration of the catalyst, methanol to oil molar ratio, reaction temperature, reaction time, and the rate of stirring were thoroughly investigated. The results revealed that the optimal conditions for synthesis of biodiesel were 0.50 wt% KOH, 8:1 methanol to oil molar ratio, 32 °C reaction temperature, 30 min of reaction, and 600 rpm rate of stirring. Under these conditions, biodiesel with a yield of 95.20 ± 2.5% w/w was obtained. ^{1}HNMR spectroscopy was used to assure the conversion of the oils blend to biodiesel. Based on ^{1}HNMR spectroscopy results, conversion of mixed CSO and WFO into biodiesel was 97.74%. The fuel properties of the resulting biodiesel were within the acceptable limits prescribed by ASTM D 6751. Furthermore, biodiesel from the said blend, have low viscosity and density comparing to those of CSO biodiesel. In conclusion, the proposed oils blend may be a profitable feedstock source, and easy way to improve biodiesel properties that synthesized from CSO.

1. Introduction

Biofuel which is made up by mono-alkyl-esters of long chain fatty acids, derived from triglycerides (vegetable oils or animal fat) is known as biodiesel (BD). It can be used as a partial or total substitute of petro diesel in compression ignition engines or for electricity generation. Transesterification process which involves the exchange of the glycerin in the triglycerides molecule by the alkyl group of the utilized alcohol which is mainly methanol or ethanol in the presence of either an acid catalyst or a base catalyst [1,2].

Many edible and non-edible feedstocks were utilized for BD production. Nonetheless, availability and cost of the oil feedstock restrict the BD production. Therefore, non-edible oil feedstocks, such as waste cooking oils [3–5], lipids from food waste [2,4], non-edible vegetable oils [6–11] and waste animal fats [2,12–15] were utilized as cheaper feedstocks for BD production were reported so as to decrease the production cost of BD. Among non-edible oils that has been received more attention as a feedstock for BD production is castor (*Ricinus communis*) seed oil, due to it is not suitable for human consumption and thus it does not compete with food crops, its high content of oil which amounts 50% in addition to the high oil yields which could reach about 1188 kg oil per hectare annually. Furthermore, the castor plant does not necessitate a great deal of maintenance or high quality water and it can grow in marginal soils. On these basis, castor oil is an attractive low cost feedstock for BD production [16].

The castor (*Ricinus communis*) plant can be found worldwide. It is wild grown in many tropical and sub-tropical countries without special care, because it can tolerate very different climate conditions. However, the castor plant agriculture have been increased in several countries, such as Brazil, China and India [17]. The oil extracted from the castor bean seed has more than 700 uses in the field of; plastics, cosmetics, manufacturing of biodiesel, lubricants and medicine [1,2]. Moreover, due to its high viscosity, it becomes a prime candidate as additive for diesel fuel to increase the lubricity of the latter. India is the largest world producer and exporter of castor oil, with about 70% of the total exports, followed by China 15%, Brazil 8% and Thailand 1%, whereas

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Nomenclature

BD	biodiesel
FAME	fatty acid methyl esters
CSO	castor seed oil
WFO	waste fish oil
CN	cetane number
HHV	higher heating value
SV	saponification value
IV	iodine value

countries such as USA, Russia and Japan are the major importers [18]. According to the National Supply Company, in Brazil, the production of castor bean fruit reached 137.1 thousand tons in the 2005/2006 harvest, and castor oil may become the main resource of oil for biodiesel production in Brazil. In Iraq, the castor plant has widely planted in addition to its presence naturally. Southern and central Iraq comprise more areas where castor is grown. Nevertheless, the castor plant can also be found in northern Iraq, such as Nineveh Governorates, Salahaldeen Governorates and Erbil Governorates. Unfortunately, exploitation of castor bean oil for industrial application is limited so far, and it is mainly produced for medical purposes.

The CSO has a unique chemical structure in comparison to other vegetable oils due to it mainly consists of Ricinoleic acid, which is characterized by containing a hydroxyl group on carbon-12, which made it the highest polarity vegetable oil. In addition, the high polarity of CSO made it possess the highest viscosity and density compared to remaining vegetable oils. The kinematic viscosity of CSO is (226 $mm^2\,s^{-1}$) at 40 °C, while the kinematic viscosity values of most vegetable oils are between 27 and 54 $mm^2\,s^{-1}$ at the same temperature [19,20]. Accordingly, the kinematic viscosity of the BD produced from the CSO is much greater than those of conventional biodiesels, and thus must be blended with other less viscosities diesel fuels (biodiesels or petro diesel fuel) to lessen its properties to the acceptable limits [21–26]. Blending of BD from the CSO with those of lower viscosities biodiesels was widely reported in literature. Meneghetti et al. [24] studied transesterification of blends of the CSO with cotton seed and soybean oils, and obtained maximum yield of BD using a blend that contains 25% soybean oil and 75% CSO. Barbosa et al. [22] investigated transesterification of mixed CSO and soybean oil with ethanol and reported that the yield of BD increased with decreasing CSO content. Besides, the viscosity of BD from the blends reduced with decreasing CSO content. Production of BD from an equivalent blend of CSO and waste chicken oil was investigated by Fadhil and Ahmed [21]. They prepared various blends of CSO and waste chicken oil, and found that the equivalent blend was the optimal feedstock for BD synthesis. Finally, Blending CSO esters with safflower methyl and ethyl esters exhibited similar reduction in viscosity [23].

Production of BD from waste animal fats is cheaper than that produced from vegetable oils, due to animal waste are greatly generated with huge amounts from slaughter houses and other meat processing industries. In addition, recovery of oils or fats from waste animal fats is cheaper than the production of oils from vegetable oils. As a result, use of waste animal fats is a significant means for solving the high production cost of BD and to decreases environmental impacts caused by their incorrect management, due to such raw materials adds value to the wastes, which otherwise need to be further eliminated. Furthermore, huge quantities of animal wastes are generated and their use as animals feed has been strongly decreased, due to the possibility of transmission of severe animal disease. BD from animal fats has higher calorific value and cetane number due to their high level of saturated fatty acids. On the other hand, BD from animal fats has several disadvantages including less stability to oxidation, due to the absence of natural antioxidants in addition to the its higher cold filter plugging and pour point values. Nevertheless, BD from animal fats might be used 100% pure fuel in boilers for heat generation or mixed with other raw materials, even improving some fuel characteristics [2,27,28].

Waste fish oil which can be obtained from discarded parts of fish is a suitable feedstock for BD production due to it can be obtained with huge amounts in addition to its very low kinematic viscosity value which could produce a BD fuel with a kinematic viscosity lower than those reported in literature for biodiesels form various animal fats and vegetable oils [2]. Nonetheless, blending of CSO with WFO to produce BD fuel with properties conformed to those prescribed by ASTM standards has not yet been reported in the literature to best of the authors knowledge.

Production of BD from mixed CSO and WFO through base-catalyzed transesterification with methanol is the main target of the present investigation. Different blends of CSO and WFO were prepared and their properties were evaluated to select the optimal oils blend that is having properties closer to those reported for oils used in BD synthesis. Optimization of transesterification parameters of the optimal oils blend were optimized. The fatty acid composition of the CSO, WFO and their equivalent blend was determined. In addition, The ^{1}H NMR spectroscopy was used to monitor the conversion of the said blend to BD and to determine the quality of the resulting BD as well. The fuel properties of the obtained biodiesel were determined following the ASTM standards.

2. Experimental

2.1. Materials and reagents

The castor seeds were collected from the lands located in the city of Mosul, Nineveh Governorates, while the fish waste was collected from fish Slaughterhouse located in Salahaladeen Governorates during the summer of 2013. Methanol (98.0%), Analytical grade isopropyl alcohol (99.8%), n-hexane (96%), anhydrous sodium sulfate (Na_2SO_4 99%), iodine (pellets), acetone, and diethyl ether were purchased from BDH (UK). Chloroform, potassium hydroxide (KOH, pellets), sodium hydroxides (NaOH, pellets), sodium methoxide (CH_3ONa) and sodium ethoxide (CH_3CH_2ONa) were obtained from Fluka (Germany).

2.2. Preparation of feedstocks

The castor seeds were cleaned and oven-dried at 50 °C for 24 h to be ground later by an electrical grinder. The oil was extracted by n-hexane in a Soxhlet extractor for 10 h, followed by distillation under vacuum using a rotary evaporator to separate the oil from the solvent. The obtained oil was dried over anhydrous sodium sulfate to eliminate the residual moisture, filtered and finally kept in a sealed container at 5 °C for further assessment and use. The yield of the oil was calculated, on dry bases [9,10].

Discarded parts of *Cyprinus carpio* fish (head, tails, backbones, fatty layer and skin) were used as source for fish oil. Extraction of fish oil was conducted following procedure given elsewhere [2]. In brief, the fish waste was transferred to a 1 L conical flask and heated by means of a boiled water bath. The resulting fish oil was placed into a separating funnel and left for 24 h for water separation, followed by filtration and finally drying over anhydrous sodium sulfate. The pure fish oil was kept in a dark place for subsequent assessment and use.

2.3. Preparation and characterization of CSO, WFO and their blends

The CSO and WFO were mixed and utilized in BD production. Different blends of CSO and WFO (10, 20, 30, 40 and 50% CSO:WFO w/w) were prepared through mixing CSO with WFO using a mechanical stirrer for 30 min to obtain homogeneous mixture. Later on, several physical and chemical properties of the parent oils and their blends including the density at 15.5 °C, the kinematic viscosity at 40 °C, flash point, the acid value, the refractive index and the pour point were