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Potassium acetate supported on activated carbon for transesterification of new non-edible oil, bitter almond oil

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HIGHLIGHTS

- Potassium acetate was loaded on PET derived activated carbon and used as solid base catalyst.
- The developed catalyst was used for transesterification of new non-edible oil, bitter almond oil.
- Biodiesel was produced with 93.21% efficiency and a purity of 97.01% w/w.

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ABSTRACT

Fatty acid methyl ester (biodiesel) was developed from new non-edible feedstock oil, bitter almond oil (BAO) through transestefication with methanol using potassium acetate supported on activated carbon (PA/AC) as a solid base catalyst. Activated carbon was prepared from waste of polyethyleneterphathalte, then the activated carbon was loaded with potassium acetate to prepare the heterogeneous solid base catalyst. Variables affecting yield of biodiesel such as, amount of potassium acetate impregnated in the activated carbon, amount of the catalyst, methanol to oil molar ratio, reaction temperature and reaction time, were investigated to optimize the reaction conditions. The biodiesel with the best yield (93.21 with an ester content of 97.01% w/w) and properties was obtained by using the catalyst loaded with 33.60 wt.% of potassium acetate, 2.50% w/w of the solid catalyst, 9:1 methanol to oil molar ratio, 65 °C reaction temperature and 150 minutes of reaction. Properties of the prepared biodiesel exhibited that PA/AC is an effective solid base catalyst for the conversion of BAO into more valuable fuel. Moreover, properties of biodiesel were within the recommended biodiesel standards as prescribed by ASTM D 6751. The Fourier Transform Infra-red spectroscopy was used to ensure the conversion of BAO into biodiesel. Transesterification of BAO using the prepared solid base catalyst was found to fellow first order kinetics and the activation energy was calculated to be 56.74 kJ/mol. The developed catalyst could be used up to four cycles with good conversion.

1. Introduction

Homogeneous – catalyzed transesterification was reported as the best process to produce biodiesel (BD). Catalysts used in transesterification process are potassium or sodium hydroxide, sodium or potassium-methoxide as well as potassium ethoxide. Alkali-catalyzed transesterification requires lower energy and shorter time to produce maximum yield of BD as well as it can be conducted at the atmospheric pressure. However, there are some problems associated with alkali-catalyzed transesterification such as its sensitivity to the presence of high content of free fatty acids in the oil or fat, which results in the formation of soaps. As a result, free fatty acid content of the oil must be reduced to the acceptable limit for base-catalyzed transesterification, either through esterification with methanol using an acid catalyst or via esterification with glycerol. However, those processes raise the production cost as well as it produces huge amount of the polluted water [1–5]. Heterogeneous catalysts were used as alternatives to homogeneous catalysts so as to overcome problems associated with latter. Heterogeneous catalysis involves the use of two types of catalysts, solid alkali catalysts and alkali supported catalysts. Among solid basic catalysts, calcium oxide and zinc oxide were widely used as heterogeneous solid catalysts in BD synthesis, but the latter shown higher activity than the former [6–8]. Moreover, modified CaO solid catalysts were also used as heterogeneous catalysts in the preparation of BD [9–11]. Highly surface area adsorbents loaded with various alkali catalysts such as KOH/Al_2O_3, KOH/NaY and

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Alumina/silica supported K_2CO_3 were used as solid basic catalysts in the production of BD from various vegetable oils as well [12,13]. Due to the high surface area of activated carbon; its use as a catalyst supporter was widely applied in various phases (liquid and vapor) reactions. Moreover, activated carbons can durable high pressure and temperature because its adsorptive characteristics are not affected greatly by the high temperature and pressure [14]. Activated carbon supported alkali base catalysts was used as a heterogeneous solid base catalyst in the process of transesterification [14–16]. Buasria et al. [17] reported transesterification of waste frying oil for synthesizing BD by KOH supported on coconut shell activated carbon in packed bed reactor. Potassium hydroxide catalyst supported on palm shell activated carbon was effective for transesterification of palm oil to fatty acid methyl ester [14]. Activated carbon supported calcium oxide catalyst was used as a solid base catalyst for transesterification of palm oil to biodiesel with a conversion of 80.98% of palm oil to fatty acid methyl esters [15]. Hameed et al. [16] used activated carbon supported potassium fluoride as a solid base catalyst for methyl esters production from waste cooking oil and reported a conversion of 83.0% of waste cooking oil to fatty acid methyl esters. The high production cost of BD is mainly attributed to the high price of the raw material. Consequently, non-edible oils, waste cooking oils and animal fats were used as potential sources for the production of BD [18–22]. Production of BD from non-edible oils has many advantages such as, they are not edible by humankind, can be found in waste lands and it can undertake severe conditions such as dryness and drought as well as it does not need any care [18–22]. It is well known that there are two types of almond, the first is the sweet almond which is characterized by its white flowers, while the second is bitter almond which its flowers is pink. Bitter almond belongs to Rosacea family. Both types of almond are found as trees and spread worldwide. It can be found in the Middle East countries such as Iran and Iraq as well as North America and Spain [20]. In Iraq, it is widely spread in the North and can be found naturally at the mountains. Furthermore, it was also cultivated so as to use its oil as a medication. High yield of oil could be obtained from bitter almond seed. Moreover, the oil is non-edible because it contains three major compounds which are, Benz aldehyde, glycoside amygdaline and hydro cyanide. The presence of hydro cyanide makes the crude bitter almond oil poisonous so that a dosage of 7.7 mL results in death. Thus, precaution must be taken in the consideration when BAO is used as a medication. It was reported that BAO is widely used for skin care as well as it can be used as anti-fever and anti-cancer medication.

Consumption of polyethyleneterphathalte (PET) was increased due to its use in various uses such as soft drinks bottles. As a result, huge amounts of such solid waste were accumulated resulting in a serious environmental pollution due to its low bio- and photo-degradability. Conversion of PET waste to activated carbons was one of the solutions that was proposed to get rid of such non-biodegradable waste. Many studies were reported on the use of PET waste as a precursor in activated carbon preparation [23–25]. As we stated above, the use of activated carbons as catalyst supporters was reported. However, most of those activated carbons were produced from feedstocks which are not available worldwide, namely palm and coconut shells [17,26]. When we reviewed the literature, we found no literature on the use of AC produced from PET waste as a catalyst supporter or as a solid base catalyst for BD production. Moreover, no literature was reported on the use of PA/AC as a solid base catalyst for BD production from any edible or non-edible oil. Furthermore, synthesis of BD from BAO via heterogeneous-catalyzed transesterification was not reported by any researcher.

The present research work was undertaken to investigate conversion of new non-edible feedstock oil, bitter almond oil to its fatty acid methyl ester (biodiesel) using an efficient solid base catalyst, *i.e.* potassium acetate loaded on PET derived activated carbon. The optimization of the process parameters such as amount of potassium acetate loaded on the AC, amount of the solid base catalyst, methanol to oil molar ratio, temperature and time were investigated. Recycling and evaluation of the spent catalyst was also investigated. The fuel properties of BD produced from BAO were determined in accordance with ASTM standards. Quality of the produce BD was analyzed by FTIR spectroscopy. Finally, kinetics of transesterification of BAO with methanol using the prepared solid catalyst was investigated as well.

2. Experimental

2.1. Materials

Bitter almond seed was collected from tress located in the city of Dohuk Governorate, North of Iraq. Used transparent plastic water bottles produced from PET were collected from the university restaurant. Methanol (reagent grade), hexane, diethyl ether, acetic acid and iodine were supplied from BDH (UK). Potassium acetate was supplied from Fluka. All chemicals were of analytical reagent grade and were used as received without any further purification.

2.2. Extraction of the oil

Seeds of bitter almond were collected and sunlight-died for two days. The dried seeds were then ground using an electrical grinder. Extraction of oil was performed using n-hexane as a solvent in a Soxhlet extractor connected with a 1 L round bottomed flask. After the extraction was over (10 h), the oil was separated from hexane by using a rotary evaporator. The obtained oil was dried by mixing with freshly activated sodium sulphate (Na_2SO_4) to eliminate the residual moisture [19]. Finally, the oil was filtered, transferred to a dark container, and was kept at 5 °C for further assessment and use. Yield of the oil was calculated on dry bases as follows:

$$\text{Yield } (\%\text{w/w}) = \frac{\text{Wt. of oil extracted (g)}}{\text{Wt. of dry seeds used (g)}} \times 100$$

Properties of BAO used in the present study were measured in accordance with the ASTM standards. The iodine value of BAO was measured using Hanus method.

2.3. Preparation of the activated carbon

Consumer soft-drink bottles (PET) were cut into small pieces (1–3 mm). The pieces were then fed to a tubular reactor provided with a thermo couple and heated by an external electrical furnace. The reactor was heated gradually from room temperature to a final temperature of 500 °C under an atmosphere of nitrogen gas at a heating rate of 10 °C per minute until gases were no longer evolved (1 h). The produced char was then crushed and allowed to pass through a 600 μm sieve. Then, it was converted to activated carbon (AC) so as to increase its porosity and surface area. A given weight of the char was transferred to a quartz tube. The tube was then placed into a tubular furnace, and the activation process was conducted at 750 °C under a flow of steam for 90 min [27]. The produced AC was crushed and sieved to obtain mean particle size of (140 μm) and kept in a desiccator until use.

2.4. Preparation of the catalyst

A three necks round bottom flask, provided with a reflux condenser and a mechanical stirrer was used as a reactor set up for