Optimization of methyl esters production from non-edible oils using activated carbon supported potassium hydroxide as a solid base catalyst

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ABSTRACT
The present investigation reports transesterification of non-edible oils, waste cooking oil (WCO) and waste fish oil (WFO) with methanol using activated carbon supported potassium hydroxide (KOH) as a solid base catalyst. Activated carbon was prepared from polyethylene terephthalate waste and loaded with KOH by wet impregnation method to prepare KOH/AC composite. X-ray diffraction and Scanning Electron Microscopy (SEM) were utilized to characterize the resulting solid base catalyst. Retention method was utilized to measure the specific surface area of the activated carbon and its derived solid base catalyst, while Hammett indicator method was followed to determine the basic strength of the prepared solid base catalyst. The prepared catalyst has granular and porous structures with a high basicity and a superior catalytic performance for the transesterification reaction. Transesterification reaction variables were arranged to obtain the best biodiesel yield. The highest methyl ester yield from WCO (88.12% w/w with an ester content of 96.68% w/w) was obtained by employing 3.5 wt.% KOH/AC catalyst, 9:1 methanol to oil molar ratio, 65 °C reaction temperature, the reaction time of 180 min and the stirring rate of 600 rpm, while maximum methyl ester yield from WFO (92.66% w/w with 96.98% w/w ester content) was produced with 3.0 wt.% KOH/AC catalyst, 9:1 methanol to oil molar ratio at 65 °C for 150 minutes of the reaction and 600 rpm. The prepared solid base catalyst was recoverable and thermally stable giving a yield of 70 wt.% after the 5th cycle. The fuel properties of the raw oils were significantly enhanced after transesterification with methanol in the presence of KOH/AC, and were in conformity with the ASTM D 6751 limits as well. Therefore, the prepared KOH/AC composite may be considered as a promising solid base catalyst for transesterification of non-edible oils with methanol.

1. Introduction
Biodiesel (BD) is a renewable, biodegradable and sustainable liquid bio-fuel. It can typically be produced from triglycerides (vegetable oils or animal fats) through base-catalyzed transesterification reaction with methanol or ethanol (Takase et al., 2014). BD is an effective alternative to petro diesel fuel. It can be blended with diesel fuel or used in a pure form. The use of BD as a fuel reduces pollutant levels and probable carcinogens produced upon combustion of fossil based fuels (Encinar, González, Pardal, & Martínez, 2010; Li et al., 2013; Takase et al., 2014). However, the high price of BD could be ascribed to the highly expensive raw materials used in its production. BD production through homogeneous catalysis also increases its production cost due to soap formation, non-reusability of the catalyst, and handling and separation problems. Consequently, heterogeneous catalysis was applied at a commercial level because of its advantages, such as ease of separation from the reaction mixture, selectivity, and appreciable catalytic activity in reuse. Heterogeneous catalysis brings up some problems, such as the mass transfer diffusional resistance which decreases the reaction rate to a large extent in comparison to homogeneous catalysis. To overcome this problem, catalyst support which can provide higher surface area and high number of the active sites was utilized in transesterification reaction of oils or fats to yield their corresponding fatty acid alkyl ester (Dhawane et al., 2016; Kaur & Ali, 2014; Zabeti, Daud, & Aroua, 2009).

Metal oxides and modified metal oxides were used as catalysts in various applications, such as photocatalytic degradation reactions of industrial dyes (Puna et al., 2013; Puna et al., 2014; Saravanan, Gracia, et al., 2015; Saravanan, Gupta, et al., 2015; Saravanan, Khan, et al., 2015; Saravanan et al., 2016) as well as preparation of nanoparticles modified electrode for the determination of drugs (Devaraj et al., 2016). They were also used as solid base catalysts for synthesis of biodiesel.
Alumina, alumina/silica, CaO, MgO and NaY were tested as supports for different alkali salts, like KOH, NaOH, KF and K₂CO₃. However, using activated carbon as a catalyst support is highly effective in both liquid and vapor phase reactions. Activated carbon has higher micro-porous surface and larger active sites than the other adsorbents making it a suitable catalyst support for the impregnation of base catalysts. Different catalysts, such as potassium carbonate, ferrous sulfate, potassium hydroxide, calcium oxide, and potassium fluoride were easily dispersed on the support surface to enhance the transesterification reaction (Baroutian et al., 2010; Dias et al., 2013; Hindryawati et al., 2011). High surface area activated carbons were prepared from polyethylene terephthalate waste (soft drink bottles) following the procedure given previously by Fadhil and Ahmed (2016). The average molecular weight of the oils was calculated based on their fatty acid compositions. The acid values of the raw oils were determined by the titration method following ASTM D664 test methods, whereas their iodine values were measured as per Hanus method.

2. Materials and methods
2.1. Materials
Waste cooking oil (WCO) and fish waste were obtained from restaurants and fish slaughterhouse, respectively run in the city of Mosul, Nineveh Governorate, north of Iraq in August 2013. Polyethylene terephthalate waste (consumed transparent plastic water bottles) were taken from the university restaurant and used in the preparation of the activated carbon (AC). Reagent grade methanol (99%) and potassium hydroxide were purchased from BDH (UK). Other chemicals were obtained from Merck (Kenilworth, NJ). All chemicals were of analytical reagent grade and used as received without any further purification.

2.2. Preparation of feedstocks
Waste cooking oil was mixed with anhydrous sodium sulfate and left overnight for moisture removal. The oil was then filtered to remove particles of sodium sulfate and kept in a dark container for further use. The waste fish oil (WFO) was extracted from fish waste as explained elsewhere (Fadhil & Ahmed, 2016). The average molecular weight of the oils was determined by the titration method following ASTM D664 test method, whereas their iodine values were measured as per Hanus method.

2.3. Preparation of the activated carbon and KOH/AC solid catalyst
The AC was prepared from the polyethylene terephthalate waste (soft drink bottles) following the procedure given previously by Fadhil and Ahmed (2016). Briefly, PET waste was cut, carbonized at 500°C and steam activated at 750°C (Fadhil & Ahmed, 2016). The KOH/AC solid base catalyst was prepared by wet impregnation method. The AC was immersed in KOH solutions of different concentrations (25–100%). The impregnated samples were stirred for 6 h at 600 rpm. After impregnation, the mixture was filtered using a filter paper (Whatman No.1) and oven-dried at 105°C until a constant weight was obtained. The dried catalysts were calcined at 450°C for 2 h. The amount of KOH loaded on the AC was determined gravimetrically (Fadhil, Al-Tikrity, & Albadree, 2015; Wan & Hameed, 2010).

2.4. Characterization of the catalyst
Scanning Electron Microscopy was utilized using a FEI Quanta 200 FEI Co. Ltd. at the accelerating voltage of 20-kV to investigate the morphologies of the AC and the solid base catalyst derived from it. X-ray
differactograms obtained using a reflection scan with nickel-filtered CuKα radiation at 40 kV and 70 mA (PW 3040/60 X’PERT PRO ANALYTICAL 2009, The Netherlands) were used to analyze the crystal structure of the newly prepared solid catalyst. The measurements were performed at (2θ) between 20° and 80°. The specific surface areas of the activated carbon and the catalyst were determined by the retention method (Fadhil & Saeed, 2016). The basic properties of the catalysts were evaluated by amine titration using Hammett indicators (Tabak et al., 2007; Takase et al., 2014).

2.5. Transesterification of non-edible oil using KOH/AC solid base catalyst

Transesterification experiments of the non-edible oils with methanol using the prepared solid base catalyst were performed in a (250 mL) three-neck round-bottom flask with a condenser and a thermometer. The round was filled with (50g) of the oil. The catalyst was mixed with the appropriated amount of methanol and then added to the oil. The mixture was refluxed with stirring at 600 rpm for a given reaction time. As the reaction was completed, the catalyst was separated from the reaction mixture through centrifugation. The filtrate was transferred to a separating funnel and allowed to settle, to ensure the separation of the methyl esters and glycerol completely. After removal of the glycerol, excess methanol was recovered from the methyl ester layer by distillation under vacuum using a rotary evaporator. The methyl content on the purified BD, was determined by column chromatography following method proposed by (Bindhu et al., 2012). A glass column (18 × 46 cm) packed with silica gel (60–120 mesh) was loaded with (1.0 g of BD) dissolved in hexane. The methyl ester fraction was eluted with (300mL) of a mixture of (hexane: diethyl ether 99.5:0.5% v/v). After evaporation of the solvent system, amount of methyl esters separated was calculated and the ester content was determined on a weight bases. The BD yield was calculated by the following equation:

\[
\text{BD yield} \ (%) = \frac{\text{Weight of the product} \times \text{Ester content} \ (%)}{\text{Total weight of oil used} \ (g)} \times 100
\]

2.6. Analysis and characterization of biodiesel

The fuel properties of the methyl esters including the flash point (D93), cloud point (ASTM D 2500), pour point (ASTM D 97), kinematic viscosity at 40 °C (ASTM D445), density at 15.6 °C (ASTM D 5002), acid value (ASTM D664), refractive index at 20 °C (D1747 – 09) and carbon residue (ASTM D 4530) were determined. AOCS Cc 17-95 was followed to determine the soap content of the prepared biodiesel, whereas (Pisarello, Dall-Csta, Veizaaga, & Querini, 2010) was used for determining the total and free glycerin in the produced methyl esters. Each property was measured in triplicate and the result was presented as the mean ± standard deviation (SD).

2.7. Regeneration and reusability of the catalyst

Regeneration of the resulting solid base catalyst was performed in a Soxhlet apparatus using a mixture of hexane and acetone so as to remove BD, glycerol and the oil molecules attached to the catalyst surface. After the regeneration, the regenerated catalyst was tested for transesterification of the non-edible oils with methanol using the optimal conditions obtained during the study (Fadhil et al., 2016a, 2016b).

3. Results and discussion

3.1. Feedstocks properties

As we stated earlier, different non-edible oils were utilized for BD production using the solid base catalyst. Considering WCO, in Iraq, sunflower oil is the main vegetable oil used for cooking and frying. The acid values of WCO and WFO were found to be 2.0 and 1.23 mg KOH/g, respectively. In consequence, one-step transesterification reaction of both oils with methanol using the prepared solid base catalyst is possible.

3.2. Selection of the optimal catalyst and its analysis

The amount of KOH loaded onto the AC increased with increasing KOH concentration in the impregnation solution as shown in Table 1. In addition, the surface of the AC decreased with increasing the amount of KOH loaded on the AC. However, the solution which contains 75 wt.% of KOH exhibited the highest loading of KOH on the AC. Furthermore, this sample showed the lowest surface area among all the samples, due to the blocking of the AC pores with KOH molecules (Fadhil et al., 2016b). It is also clearly seen from Table 1 that the increase in the amount of KOH in the impregnation solution led to an increase in the basic strength of the catalyst. The highest basicity (9.3 < H<sub>b</sub> < 15) of KOH/AC catalyst was obtained with the sample which contains 75 wt.% KOH in the impregnation solution (a loading of 28.75% w/w). Beyond this concentration, no significant increase in the basic strength of the catalyst was observed. Transesterification of WCO and WFO was carried out using 3.0% w/w of the catalyst, 6:1 methanol to oil molar ratio, 60 °C reaction temperature, 120 minutes of reaction and 600rpm rate of stirring under optimum conditions selected for KOH/AC catalyst as shown in Table 1. The methyl ester yield increased in parallel
with the amount of KOH loaded on the AC. The cata-
ylist loaded with the highest amount of KOH (28.75% w/w) resulted in the highest conversion for both oils. Consequently, the catalyst loaded with 28.75% w/w KOH was chosen as the best catalyst, and thus it was utilized in the next transesterification experiments.

In order to characterize the phase and the structure of this KOH/AC solid base catalyst, the XRD analysis of the catalyst was conducted as shown in Figure 1. The X-ray diffractograms of the AC showed broad diffraction peaks at 2\(\theta\) = 24.24\(^{\circ}\) and 43.43\(^{\circ}\) which are ascribed to the typical amorphous carbon with polycyclic aromatic sheets. They also indicate the destruction of the PET and generation of the randomly arranged amorphous carbon structures during carbonization and activation. After the KOH loading, many peaks appeared at different positions (2\(\theta\) = 23.97\(^{\circ}\), 30.26\(^{\circ}\), 34.33\(^{\circ}\), 35.31\(^{\circ}\), 38.15\(^{\circ}\), 39.84\(^{\circ}\), 41.49\(^{\circ}\), 44.36\(^{\circ}\), 48.31\(^{\circ}\), 53.64\(^{\circ}\) and 54.08\(^{\circ}\)). The peaks observed at 2\(\theta\) = 30.26\(^{\circ}\), 41.49\(^{\circ}\) and 53.64\(^{\circ}\) indicate the presence of \(K_2O\) phase (Li et al., 2013).

Figure 2 shows the SEM images of the parent AC and the solid base catalyst derived from it. The SEM image indicates many micropores present on the surface of AC which are produced as a result of the steam activation. The micropores on the AC surface provide high surface area of the adsorbent. It is also clear from the SEM image of the AC that the steam activation was able to build the pores on the carbon surface which is necessary for loading the catalyst molecules. The SEM image of the derived catalyst shows that the micropores on the carbon surface were blocked by the KOH molecules, which confirms that KOH molecules were significantly adsorbed onto the AC surface, suggesting that the obtained solid enables the heterogeneous-catalyzed transesterification process to proceed for BD synthesis.

### 3.3. Optimization of transesterification parameters

The low acid values of the tested non-edible (WCO and WFO) enabled direct development of BD through KOH/AC-catalyzed transesterification reaction. Therefore, the process parameters, such as the amount of the solid base catalyst, methanol to oil molar ratio, the temperature and the duration of the transesterification process were optimized. Transesterification of WCO and WFO using KOH/AC catalyst was investigated by testing different amounts of the catalyst ranging from 1.0 to 5.0% wt.% where increments by 0.50% were applied as depicted in Figure 3(a). The molar ratio of methanol to oil, temperature, time and the stirring rate of the reaction were arranged as 6:1, 60\(^{\circ}\)C, 120 minutes and 600rpm, respectively. It was observed that the methyl ester yield increased progressively with increasing the amount of the catalyst due to the higher the amount of the catalyst provides more number of the active centers, which in turn resulted in higher conversion. However, transesterification of WCO by the said solid catalyst required (3.5% w/w) of the catalyst to produce maximum yield of methyl ester comparing to WFO which exhibited the highest yield of methyl ester at (3.0% w/w) of the catalyst. This difference in the optimum amount of the catalyst necessary for achieving maximum conversion of various feedstocks could be ascribed to the acid values of the raw oils as well as the type of the oil. The WFO is a virgin oil and was not subjected to any thermal treatment in comparison to WCO which was subjected to the frying process which affects the chemical composition of the oil significantly. However, the amount of the solid catalyst more than the optimum amount caused higher mass transfer resistance due to the highly viscous mixture, resulting in lower methyl ester yield (Agarwal, Chauhan, Chaurasia, & Singh, 2012; Takase et al., 2014). Findings obtained in the present study corroborate with those reported by other researchers (Agarwal et al., 2012; Fadhil et al., 2016b; Takase et al., 2014). Based on these data, the subsequent experiments were conducted using (3.5% w/w) of KOH/AC catalyst for WCO and (3.0% w/w) for WFO.

Different methanol to oil molar ratios (3:1, 6:1, 9:1, 12:1, 15:1 and 18:1) were tested on transesterification
of WCO and WFO by the KOH/AC solid catalyst Figure 3(b). The other parameters were chosen as (3.5 wt. % KOH/AC) for WCO and (3.0 wt. % KOH/AC) for WFO, 60 °C reaction temperature, 120 minutes of reaction period and 600 rpm rate of stirring. The conversion yield was found to be very low at the lower methanol to oil molar ratio (3:1) due to incompletion of the reaction as shown in Figure 3(b) (Agarwal et al., 2012; Takase et al., 2014). Since the transesterification is a reversible reaction, and the higher methanol to oil molar ratio pushes the reaction forward the products, the methyl ester yield increases progressively. In addition, methanol facilitates the solubility of phases, thus favouring a smooth reaction with limited mass transfer resistance (Girish, Niju, Begum, & Anantharaman, 2013). It was noticed that both oils have given the highest methyl esters yield at 9:1 methanol to oil molar ratio, while molar ratios higher than the optimal decreased the methyl esters yield as shown in Figure 3(b), due to the
difficulty of glycerol separation as a result of the dilution of the oil with the excess methanol, and thus reduces the methyl ester yield (Dias et al., 2013; Zabeti et al., 2009). Accordingly, the value of 9:1 was established as the optimum methanol to oil molar ratio for transesterification of both oils in the presence of the KOH/AC catalyst.

Transesterification of non-edible oils on KOH/AC was carried out at different temperatures (30, 40, 50, 60, 65 and 70°C) as shown in Figure 3(c). The catalyst amount, the methanol to oil molar ratio, the reaction period and the stirring rate were selected as 3.5 wt. % KOH/AC for WCO and 3.0 wt. % KOH/AC for WFO, 9:1, 120 minutes and 600 rpm, respectively. As shown in Figure 3(c), the lower temperatures (30–50°C) were accompanied by lower conversion, which could be ascribed to the higher viscosity of the oil at lower temperatures, causing lower mass transfer resistance among oil-methanol-catalyst phases (Dias et al., 2013; Fadhil et al., 2016b; Hindryawati et al., 2014; Takase et al., 2014; Zabeti et al., 2009). The conversion yield increased with increasing the reaction temperature and reached the maximum value at 65°C. On the other hand, the reaction temperatures higher than 65°C reduced the methyl ester yield due to the evaporation and forming bubbles of methanol, which might inhibit the interface interaction (Al-Jammal, Al-Hamamre, & Alnaief, 2016; Encinar et al., 2010; Takase et al., 2014). Thus, value of 65°C was chosen as the optimal reaction temperature based on this observation.

Because of the importance of the reaction period on the transesterification reaction from the economical point of view, transesterification of WCO and WFO was tested at different time intervals (30–210 minutes) by 30 minutes increments Figure 3(d). The catalyst amount, the methanol to oil molar ratio, the reaction temperature and stirring rate were selected as 3.5 wt. % KOH/AC for WCO and 3.0 wt. % KOH/AC for WFO, 9:1, 65°C and 600 rpm, respectively. It was observed that higher reaction time was accompanied by a higher methyl ester yield. However, WCO gave maximum methyl ester yield after 180 minutes of the reaction, whereas WFO exhibited the highest yield of methyl ester in 150 minutes time. The difference seen in the optimum reaction time necessary for achieving the maximum conversion of various feedstocks could be explained by the different acid values of the raw oils. Furthermore, WFO is a virgin oil and was not subjected to any thermal treatment in opposition to WCO which was subjected to the frying process at a higher temperature leading to significant changes in the chemical composition. It was observed that conduction of the reaction at durations longer than the optimum period reduced the methyl ester which may be due to the hydrolysis of some of the esters to their corresponding free fatty acids (Fadhil et al., 2016a, 2016b; Hindryawati et al., 2014).

3.4. Reusability of the solid catalyst

The most important characteristics of the solid base catalysts are their recoverability and reusability which in turn affect the economics of using heterogeneous catalysis for biodiesel production (Encinar et al., 2010; Fadhil et al., 2015). Based on this fact, the utilized catalyst was regenerated and examined for transesterification of WCO and WFO with methanol for further cycles (five cycles) by applying the optimum conditions obtained during the present study as shown in Table 2.

The results pointed out that the methyl ester yield was reduced by increasing the cycle number when the regenerated catalyst used. However, good conversion (>70%) was obtained up to the 5th cycle. The reduction in the methyl ester yield with increasing the regeneration runs could be attributed to the leaching of active metals from the support surface. As a result, the number of the active sites available for the reaction will be less in number. These achievements agree with the previously reported
data by other researchers (Al-Jammal et al., 2016; Girish et al., 2013; Takase et al., 2014). Moreover, deactivation of the catalyst could also be due to the adsorption of oil, methyl ester, glycerol and free fatty acids on the surface of catalyst (Girish et al., 2013).

Table 2 also presents the influence of the catalyst reusability on the acid value of the methyl ester produced using the regenerated solid base catalyst. It was also noticed that the acid value of the produced methyl ester increases with the increase of the number of recycles, which could also be ascribed to the decrease of the number of active sites available for the reaction (Fadhil et al., 2016b).

3.5. Comparison of the prepared catalyst with other solid catalysts

Table 3 compares the results obtained for the transesterification of WCO and WFO with methanol using KOH/AC solid base catalyst with other solid base catalysts prepared by the impregnation of various potassium salts onto different supports, such as the AC, zirconia, CaO, alumina, etc. The comparison shows that the amount of the potassium salt (KOH) loaded on the AC is almost higher than that observed for other solid catalysts. This could be attributed to the higher surface area of the AC than the other supports. Although the optimum reaction temperature and time obtained using the newly developed solid catalyst were comparable to many solid catalysts reported in literature; the solid base catalyst developed in the present study gave the

### Table 2. Effect of reusability of the catalysts on the yield and acid value of biodiesels.

| Cycle | WCO Yield | WFO Yield | Acid Value (mg KOH/g) |
|-------|-----------|-----------|-----------------------|
| 1     | 88.12     | 92.66     | 0.15                  |
| 2     | 85.13     | 88.04     | 0.24                  |
| 3     | 80.44     | 82.22     | 0.29                  |
| 4     | 76.2      | 76.3      | 0.36                  |
| 5     | 70.21     | 72.22     | 0.41                  |

Figure 3. Influence of (a) catalyst amount, (b) methanol to oil molar ratio, (c) reaction temperature and (d) reaction time on the methyl ester yield.
maximum yield of methyl ester with a lower amount of the catalyst and a lower methanol to oil molar ratio than the other solid catalysts. Hence, it can be considered as an attractive catalyst for making BD fuels. However, the differences in the optimal conditions required for maximum yield of BD from various oil feedstocks by using different solid base catalysts could be attributed to a number of factors, such as the acid values of raw oils utilized in the production of BD, the reactivity of the utilized solid base catalyst, the type of the ion loaded onto the support and the utilized support (carbon based catalyst, clay based catalyst, etc.) and mode of heating (conventional, microwave, or sonication) employed during the transesterification process.

3.6. Properties of biodiesels produced using KOH/AC solid base catalyst

The fuel properties of biodiesels produced from WCO and WFO by transesterification with methanol using KOH/AC solid base catalyst were measured in accordance with ASTM standard methods and the results were compared with those of standard ASTM D6751 BD (Table 4).

The density, kinematic viscosity, flash point and refractive index values of the raw oils were significantly reduced after transesterification with methanol in the presence of the solid base catalyst, which reflects the reactivity of the prepared solid base catalyst and proves that the values of the assessed properties satisfy the limits prescribed by ASTM standard.
D 6751 BD. Another evidence on the reactivity of the prepared solid base catalyst is the acid values of obtained biodiesels which are much lower than those of the corresponding raw oils. The pour points of the prepared biodiesels indicate that the produced fuels will be convenient for use in cold weather conditions. Other properties of the produced biodiesels, such as the content of the total glycerin, free glycerin, water, menthol and soaps were much lower than the standard values, which also assures the high conversion level of the utilized oils to their methyl esters in the presence of the newly prepared solid base catalyst.

Conclusions

The solid base catalyst prepared by the impregnation of activated carbon originating from polyethylene terphthalate waste with KOH was utilized for transesterification of different non-edible oils, namely WCO and WFO with methanol. KOH/AC-catalyzed transesterification of WCO gave the highest yield of methyl ester (88.12% w/w) using 3.5 wt.% of KOH/AC catalyst, 9:1 methanol to oil molar ratio, 65°C reaction temperature, 180 minutes of the reaction time and 600 rpm rate of stirring, whilst maximum methyl ester yields from WFO (92.66% w/w) was produced by utilizing 3.0 wt.% of KOH/AC catalyst, 9:1 methanol to oil molar ratio, 65°C reaction temperature, 150 minutes of the reaction time and 600 rpm rate of stirring. The properties of the produced biodiesels were very local to those of no. 2 diesel fuel which enables us to use it in the injection engines without any modification. Moreover, the catalysts were effective for at least five cycles with a yield greater than 70 wt.%.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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