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CO-SOLVENT TRANSESTERIFICATION OF BITTER ALMOND OIL INTO BIODIESEL: OPTIMIZATION OF VARIABLES AND CHARACTERIZATION OF BIODIESEL

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Abstract. The influence of co-solvent on transesterification of one of non-edible feedstocks, Bitter Almond Oil (BAO) with methanol was investigated. Hexane and potassium hydroxide (KOH) were chosen as the co-solvent and the catalyst, respectively. The variables included in the optimization process were concentration of KOH, methanol to oil molar ratio, hexane to methanol volume ratio, reaction temperature, reaction time, type of co-solvent and type of the alkali catalyst. BioDiesel (BD) with yield of 97.88 and 98.50 wt. % ester content were obtained using 0.60 wt. % KOH, 5:1 methanol to oil molar ratio, 1:1 hexane to methanol volume ratio, 32 °C reaction temperature and 45 minutes of reaction. The Fourier Transform InfraRed (FTIR) spectroscopy and Thin Layer Chromatography (TLC) were used to ensure the conversion of BAO into BD. The fuel properties of the prepared BD were determined and found within the acceptable limits prescribed by ASTM D6751-15ce1 and EN 14214:2017. Moreover, properties of (biodiesel + petro-diesel) blends complied with the limits prescribed in the ASTM D7467-17 standards as well. It was concluded that the presence of co-solvent reduced the concentration of the catalyst, temperature, methanol to oil molar ratio and time required to produce maximum yield of BD comparing to non-solvent process. As a result, co-solvent transesterification is recommended for further application.

Keywords: bitter almond oil, co-solvent transesterification, biodiesel, fuel properties, analysis of biodiesel, blending evaluation.

Introduction

Energy from biomass is one of the renewable energy sources. It was considered one of the alternatives that was used to slow down the fast depletion of fossil sources. Besides, it reduces the environmental pollution caused by the increasing combustion of fossil sources. Biomass can be converted into liquid fuels via different methods, such as pyrolysis, fermentation and transesterification. Among liquid biofuels, BioDiesel (BD) was gained more concern as a potential alternative to fossil diesel fuel. This fuel can be produced through the catalytic transesterification of vegetable oils or animal fats with short chains alcohols (methanol or ethanol) in the presence of a suitable catalyst (Anastopoulos *et al.* 2009; Cunha *et al.* 2013; Dias *et al.* 2009; Gürü *et al.* 2009, 2010; Ejikeme *et al.* 2013; Birla *et al.* 2012; Guan *et al.* 2009; Chang *et al.* 2013; Wyatt *et al.* 2005; Nuhu, Kovo 2015). Various edible oils were used for BD production, such as rapeseed, sunflower, soybean and palm oils (Encinar *et al.* 2010; Fadhil, Abdulahad 2014; Guzatto *et al.* 2012; Suppalakpanya *et al.* 2010a, 2010b; Carvalho *et al.* 2013; García *et al.* 2011; Nehdi *et al.* 2014; Zhang *et al.* 2010; Reyero *et al.* 2015). However, those oils are potential source of food for humankind. Consequently, non-edible oils, waste cooking oils and animal fats were used as potential feedstocks for synthesis of BD (Kafuku, Mbarawa 2010; García *et al.* 2011; Atapour, Kariminia 2013; Fadhil 2013a, 2013b; Fadhil *et al.* 2017b; Fadhil, Ali 2013; Gürü *et al.* 2009, 2010; Encinar *et al.* 2011; Cunha *et al.* 2013; Alptekin, Canakci 2010). The high cost of BD production is mainly attributed to the high price of the raw feedstocks used in its production. As a result, cheaper feedstocks must be used in the production of BD so as to reduce its cost of production. Non-edible oils were used as potential feedstocks for BD synthesis because they are not edible by humankind, can be found in wastelands, can undertake severe conditions, such as dryness and drought and they don't need any care (Atapour, Kariminia 2011).

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Many non-edible oils were used in the production of BD, such as *Jatropha curcas* seed oil, rubber seed oil and castor seed oil (Mohammed-Dabo *et al.* 2012; Morshed *et al.* 2011; Peña *et al.* 2009; Berchmans *et al.* 2013; Fadhil *et al.* 2017a; Shambhu *et al.* 2013). There are two types of almond; the first is the sweet almond, which is characterized by its white flowers, whereas the second is bitter almond, which flowers are pink. 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, like Iran and Iraq. Moreover, it can also be found in North America and Spain. In Iraq, it is widely spread in the North and can be grown naturally at the mountains. Furthermore, it was also cultivated in order to use its oil as a medication. Bitter almond seeds produce high yield of oil. Besides, the extracted oil is non-edible due to it contains three major compounds which are, benzaldehyde, glycoside amygdaline and hydrocyanide. The presence of hydrocyanide makes the crude Bitter Almond Oil (BAO) 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.

It is well known that miscibility between alcohol and triglyceride during transesterification is low due to variation in their chemical structures. As a result, the mass transfer between the two phases becomes a significant factor that affects the reaction rate. Thus, to enhance miscibility between the two phases, transesterification temperature is raised, but this is an energy-consumptive process (Encinar *et al.* 2010; Mohammed-Dabo *et al.* 2012; Peña *et al.* 2009). Transesterification in the presence of a co-solvent was proposed as a new technique to increase the mixing efficiency and the mass transfer between alcohol and triglyceride (Encinar *et al.* 2010; Mohammed-Dabo *et al.* 2012; Peña *et al.* 2009; Surya Abadi Ginting *et al.* 2012). The presence of co-solvent within the reaction medium increases the reaction rate by increasing the collision among the reactants molecules, resulting in better mass transfer and shorter reaction time. Many solvents, such as Tetrahydrofuran (THF), hexane, diethyl ether, acetone and acetonitrile were used as co-solvents on transesterification process (Mohammed-Dabo *et al.* 2012; Encinar *et al.* 2010; Peña *et al.* 2009). It was reported that co-solvent utilized during transesterification reaction is preferable to have boiling point near that of employed alcohol so that it could be recycled with excess alcohol at the same time (Mohammed-Dabo *et al.* 2012; Encinar *et al.* 2010). When we reviewed the literature, few works were reported on the production of BD from almond oil (Giwa, Ogunbona 2014; Abu-Hamdeh, Alnefaie 2015; Atapour, Kariminia 2011, 2013). However, only two of those works were reported on the production of BD from BAO via conventional transesterification process (Atapour, Kariminia 2011, 2013). No literature was reported on synthesis of BD from BAO through alkali-catalysed transesterification assisted by co-solvent.

Herein, transesterification of BAO with methanol in the presence of co-solvent was investigated. The influence of co-solvent on both yield and quality of the produced BD was evaluated. Variables affecting yield of BD, such as concentration of the catalyst, methanol to oil molar ratio, hexane to methanol volume ratio, temperature, time, type of co-solvent and type of the alkali catalyst were optimized. The fuel properties of the prepared BD as well as its blends with Petro-Diesel (PD) (Knothe *et al.* 2005) were measured as per ASTM standards. The produced BD was also analysed by the Fourier Transform InfraRed (FTIR) spectroscopy and Thin Layer Chromatography (TLC).

1. Experimental

1.1. Materials

Bitter almond seeds were collected from trees located in the city of Dohuk Governorate, North of Iraq. All chemicals used in the present study were of analytical reagent grade and used as received without any further purification. Methanol, potassium and sodium hydroxides (KOH, NaOH, pellets), sodium methoxide (CH_3ONa), sodium ethoxide (CH_3CH_2ONa), iodine, acetone, sodium sulphate (Na_2SO_4), petroleum ether (*b.p.* = 60…80 °C) and diethyl ether were purchased from BDH (UK). Chloroform, *n*-hexane and hydrochloric acid and cyclohexane were purchased from Fluka (Germany).

1.2. Extraction of oil from bitter almond seeds

Seeds of bitter almond were collected and sunlight-dried for two days. The dried seeds were ground using an electrical grinder. Extraction of the oil was performed using *n*-hexane as a solvent in a Soxhlet extractor connected with a 1 L round bottomed flask. After completion of the extraction, the oil was separated from the solvent via distillation using a rotary evaporator. The obtained oil was dried over freshly activated sodium sulphate (Na_2SO_4) 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 as follows:

$$\text{Oil yield [\% w/w]} = \frac{\text{weight of oil extracted}}{\text{weight of dry seeds used}} \cdot 100\%.$$

1.3. Co-solvent transesterification of BAO

Hundred grams of BAO and the calculated amount of the co-solvent (hexane) were transferred to a three-neck round bottom flask (1 L) equipped with a thermometer, mechanical stirrer and condenser. Afterwards, the catalyst reagent consists of KOH dissolved in methanol at a molar ratio of 6:1 methanol to fat was added to the round. The mixture was refluxed at 60±1.0 °C with simultaneous stirring at 600 rpm using a hot plate with magnetic stirrer for 60 minutes. After completion of the reaction, the products were transferred to a separating funnel and left overnight to obtain two layers. The glycerol layer (lower) was withdrawn and discarded, while the methyl esters layer (upper) was distillated under vacuum using a rotary evaporator to recover excess alcohol and hexane (Encinar *et al.* 2010; Ramírez-Verduzco *et al.* 2012). Then, it was purified by successive washing with warm distilled water (3×25 mL) to remove other impurities , such as remaining of the catalyst, soaps and glycerol. Finally, it was mixed with Na_2SO_4 to eliminate the residual moisture followed by filtration (Fadhil *et al.* 2014). Yield of the produced BD was determined as follows (Al-Hamamre, Yamin 2014; Surya Abadi Ginting 2012; Fadhil 2013a, 2013b):

$$\text{Product yield [wt. \%]} = \frac{\text{weight of BD produced}}{\text{weight of raw oil used}} \cdot 100\%;$$

$$\text{BD yield [wt. \%]} = \frac{\text{weight of purified BD}}{\text{weight of raw oil used}} \cdot 100\%.$$

1.4. Analysis of BD

The fatty acids methyl esters composition of BAO was determined by gas chromatography (GC, Perkin Elmer, Auto system GLX, Shelton, USA). Chromatographic separation was performed using a Supelco SP^{TM}-2380 (30 m × 0.25 mm i.d., 0.25 μm film thickness) column equipped with flame ionization detector. Helium was the carrier gas. The sample was injected in a flow rate of 0.5 mL/min. The injector temperature was 280 °C, and the detector temperature was 260 °C. The initial temperature of the oven was 120 °C for 2 min, increased at 5 °C/min to 220 °C, held for 10 min. Data collected and quantified with a total Chrome Navigator and the results were expressed as percent concentration (Fadhil, Abdulahad 2014). The ester content on the purified BDs was determined according to the method proposed by Bindhu *et al.* (2012). The TLC was used as a fast mean to ensure transesterification of BAO. Silica gel plates (3×10 cm glass) was washed by methanol to remove the adsorbed impurities and then activated in an oven for 2 h at 110 °C. Then, the raw oil or the fatty acid methyl esters was diluted in *n*-hexane, and spotted on the TLC plates with a capillary tube. The plates were developed (eluted) in a solvent system of hexane/ethyl ether/acetic acid (80:20:1, vol/vol/vol). After the fractionation, the solvent was evaporated and the TLC plate was visualized by iodine vapor (Fadhil *et al.* 2014; Fadhil, Ali 2013). The key functional groups on the parent oil as well as the prepared BD were determined using FTIR spectrophotometer (Biotechnology, UK). The KBr cell was used for this purpose. Prior to collection of spectrum, the cell was cleaned by successive treatments with isopropanol. The FTIR spectrum was measured within a range of 400 to 4000 cm^{-1} with 4 cm^{-1} resolution.

1.5. Testing and evaluation of fuel properties

Properties of the produced BD were evaluated as per the ASTM procedures. The density was measured according to ASTM D4052-16 using a calibrated pycnometer. The kinematic viscosity was measured based on ASTM D455-69(1995) using a kinematic viscometer, Canon U-tube calibrated glass viscometer. The refractive index (ASTM D1747-09(2014)) was measured using was measured using the Abbe refractometer (ATAGO, Japan) connected to a temperature controlled water bath that maintains the temperature of the refractometer at 40±0.1 °C. Determinations of the cloud and pour points (ASTM D2500-17a), Conradson carbon residue (ASTM D4530-15), the acid value (ASTM D664-17), the flash point (ASTM D93-16a) and the saponification value (ASTM D5555-95(2017)) were also performed. Method proposed by Pisarello *et al.* (2010) was used for determination of the total glycerine in the produced alkyl esters. This method is based on its oxidation to formic acid using sodium periodate, followed by a titration with sodium hydroxide. The Iodine Value (IV) was measured according to Hanus method. The cetane number was determined using a digital cetane number meter (Shatox, Russia). Soap content was determined in accordance with AOCS Cc 17-95(2017). Each property was measured in triplicate and the result was presented as the mean ± standard deviation (SD).

1.6. Evaluation of (BD + PD) blends

Different blends of the optimal BD sample with PD (10…50% v/v) were prepared and evaluated for several interesting properties including the density at 15.6 °C, kinematic viscosity at 40 °C, flash and pour points, acid value and refractive index at 20 °C (Fadhil, Ali 2013). The properties were measured according to the ASTM standard test methods (see Section 2.5).

2. Results and discussions

2.1. Properties and analysis of BAO

The oil content of bitter almond seeds (~42.0% w/w) on dry bases was relatively high compared to other vegetable seed oils, like soybeans (18…22%), palm seeds (40%) and sunflower seeds (40%) (Sivakumar *et al.* 2013). As a result, BAO can be used as a promising source of oil for BD production. Table 1 displays properties of BAO in comparision to rapeseed oil. It was found that the density of BAO was comparable to that of rapeseed oil (Encinar *et al.* 2010). The viscosity and flash point of BAO were lower than those reported for rapeseed oil (Encinar *et al.* 2010). These properties connect greatly with the content and type unsaturated fatty acids of the oil. BAO has higher pour point but lower iodine value than rapeseed oil. This difference could be attributed to the level of unsaturated fatty acids as well as type of unsaturated fatty acids of BAO compared to rapeseed oil.

The fatty acid profile of BAO (Table 2) shows that its content of unsaturated fatty acids (92.15%) is much higher than that of saturated fatty acids (7.85%). It was observed that BAO contains mainly oleic acid (46.0%), linoleic acid (18.93%) and palmitic acid (6.50%). Content of monounsaturated fatty acids on BAO is higher than that observed for rapeseed oil (Encinar *et al.* 2010). The lower iodine value and higher pour point of BAO compared to rapeseed oil may be due to the high content of polyunsaturated fatty acids of the latter compared to the former.

Table 1. Properties of BAO compared to rapeseed oil

Property	BAO	Rapeseed oil (Encinar *et al.* 2010)
Density @ 15.6 °C [g/ml]	0.9210	0.9186
Kinematic viscosity @ 40 °C [mm^2/s]	24.10	33.07
Flash point [°C]	180.0	246.0
Acid value [mg KOH/g oil]	0.90	1.02
Saponification value [mg KOH/g oil]	172.0	170.4
Iodine value [100 mg I_2/g oil]	93.22	108.0
Cloud point [°C]	–3.0	–
Pour point [°C]	–7.0	–19.0

2.2. Alkaline-catalysed transesterification of BAO using hexane as a co-solvent

The free fatty acid content of an oil should be between (3…5% w/w) so as to produce high yield of BD using base-catalysed transesterification (Sinha *et al.* 2008). The acid value of BAO used in the present study is 0.90 mg KOH/g, which is much lower than the acid values of rubber seed oil (90.0 mg KOH/g) and *Jatropha curcas* seed oil (29.60 KOH/g), which their use for synthesis of BD required two-step process, namely acid-base catalysed transesterification (Morshed *et al.* 2011; Mohammed-Dabo *et al.* 2012; Berchmans *et al.* 2013). As a result, no pretreatment such as an acid treatment is required to produce BD from BAO. Variables affecting the co-solvent transesterification of BAO were investigated. For comparison, BD was also produced from BAO via optimized conventional process.

Table 2. Fatty acid composition of BAO compared to rapeseed

Fatty acid (FA) composition	BAO	Rapeseed oil (Encinar *et al.* 2010)
C_{14}	0.05	0.07
$C_{14:1}$	–	–
C_{15}	0.01	–
C_{16}	6.50	4.92
$C_{16:1}$	0.58	0.24
C_{17}	–	–
C_{18}	1.20	1.63
$C_{18:1}$	72.53	66.59
$C_{18:2}$	18.93	17.08
$C_{18:3}$	0.03	7.75
C_{20}	0.06	–
$C_{20:1}$	0.06	–
C_{21}	0.01	–
C_{22}	0.02	–
Others	–	1.72
Total saturated FA	7.85	6.62
Total unsaturated FA	92.15	91.66
Total polyunsaturated FA	18.96	24.83
Total monounsaturated FA	73.19	66.83

2.2.1. Influence of the catalyst concentration

Influence of the catalyst concentration on the transesterification of BAO in the presence and absence of hexane was investigated by varying concentration of KOH from 0.20 to 1.40 w/w of oil in which 0.20% increments were used as shown in Figure 1. On co-solvent transesterification, methanol to oil molar ratio, hexane to methanol volume ratio, temperature, time and stirring rate were fixed at 6:1, 1:1, 60 °C, 60 minutes and 600 rpm, respectively. It was observed that yield of BD increases with increasing concentration of KOH for both processes. Moreover, yield of BD produced via co-solvent process was higher than that produced through non-solvent process, using the same concentration of the catalyst. Co-solvent transesterification exhibited maximum yield of BD (92.22…91.24% w/w ester content) at 0.60% KOH w/w compared to 1.0% KOH w/w for non-solvent process. This difference in the optimal concentration of KOH required for maximum conversion between the two processes may be attributed to the presence of co-solvent, which makes the reaction mixture more homogeneous and increases the mass transfer among the reactants molecules, and hence increases the reaction rate. However, addition of excess amount of catalyst results in the formation of an emulsion, which in turn increases viscosity of the product due to formation of gels. Thus, the yield decreases (Morshed *et al.* 2011; Fadhil, Ali 2014). Therefore, 0.60% KOH w/w was selected as the optimal concentration.

2.2.2. Influence of methanol to oil molar ratio

Alcohol to oil molar ratio is one of the most important variable affecting transesterification of oil into the corresponding ester. The stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1. However, this ratio is insufficient to drive the reaction to completion. Thus, using higher molar ratios are required to drive the reaction to the right. Moreover, alcohol to oil molar ratio affects the production cost. Thus, it must be optimized. Different methanol to oil molar ranged from (3:1…10:1) were tested o as to select the optimal molar ratio as shown in Figure 2. In all experiments, other factors were fixed at 0.60% KOH w/w, 1:1 hexane to methanol volume ratio, 60 °C reaction temperature, 60 minutes of reaction and 600 rpm rate of stirring. It was observed that yield of BD prepared via co-solvent transesterification was higher than that produced through non-solvent process using the same molar ratio of methanol. Moreover, co-solvent process produced the highest yield of BD (94.55…94.02% w/w) at 5:1 methanol to oil molar ratio compared to 7:1 for non-solvent transesterification. This could be ascribed to presence of co-solvent, which reduces viscosity of the oil due to dilution effect and thus increases the mass transfer between the oil and methanol resulting in better conversion. Atapour and Kariminia (2011) investigated methanolysis of BAO using different methanol to oil molar ratio and found that 9:1 was the optimal. Nevertheless, methanol to oil molar ratio higher than the optimal caused difficulty in glycerol separation and resulted in the formation of soaps. Thus, the yield decreased. Moreover, it increases cost of methanol recovery (Mohammed-Dabo *et al.* 2012; Suppalakpanya *et al.* 2010a, 2010b; Atapour, Kariminia 2011). Our findings of obtaining the best yield of BD at lower methanol to oil molar ratio is a very important finding from an economical point of view due to it reduces cost of production. Therefore, 5:1 was established as the optimal methanol to oil molar ratio.

2.2.3. Influence of hexane to methanol volume ratio

The influence of hexane to methanol volume ratio on co-solvent methanolysis of BAO was investigated by testing different hexane to methanol volume ratio (0.5:1, 1:1, 1.5:1, 2:1, 2.5:1 and 3:1) as displayed in Figure 3. Other variables were fixed at 0.60% KOH w/w, 5:1 methanol to oil molar ratio, 60 °C reaction temperature, 60 minutes of reaction and 600 rpm rate of stirring. Results in Figure 3 show that yield of BD increased from 87.0 to 94.55% as hexane to methanol volume ratio increased from 0.5:1 to 1:1. This could be ascribed to the fact that addition of higher amounts of hexane is required to overcome the mass resistance due to poor miscibility of hexane in methanol and other properties associated with its volatility. Therefore, the conversion increases (Alhassan *et al.* 2014). However, hexane to methanol volume ratios higher than the optimal reduced yield of BD. This probably occurs due to the fact, that too much hexane will dilute the reactants and thus decrease the reaction rate. Based on these results, 1:1 hexane to methanol volume ratio was fixed in subsequent experiments.

2.2.4. Influence of reaction temperature

Transesterification process is greatly affected by variation of the temperature due to it affects the production cost and reaction rate as well (Sivakumar *et al.* 2013). It was reported that due to the chemical properties of solvents included in the reaction, temperatures closer to the boiling point of methanol is favoured for transesterification reaction. If the process was conducted at temperatures higher than the boiling point of methanol, the BD yield decreases due to evaporation of methanol. However, this depends greatly on fatty acids composition of the raw material used i.e. reaction temperatures closer to the boiling point of methanol was favoured for conversion of animal fats into BD due to their high content of saturated fatty acids (Sbihi *et al.* 2014). Transesterification of BAO in the presence and absence of co-solvent was conducted at various temperatures (32, 40, 50, 60 and 70 °C) as displayed in Figure 4. Other experimental conditions were fixed at 0.60% KOH w/w, 5:1 methanol to oil molar ratio, 1:1 hex-

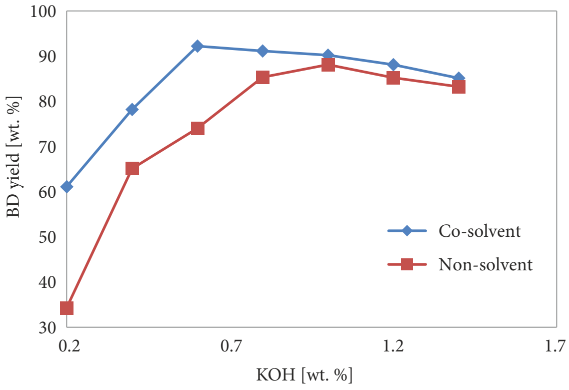

Figure 1. Influence of KOH concentration on BAO conversion

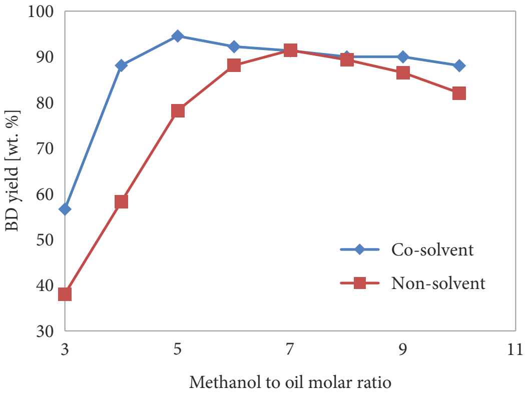

Figure 2. Influence of methanol to oil molar ratio on BAO conversion

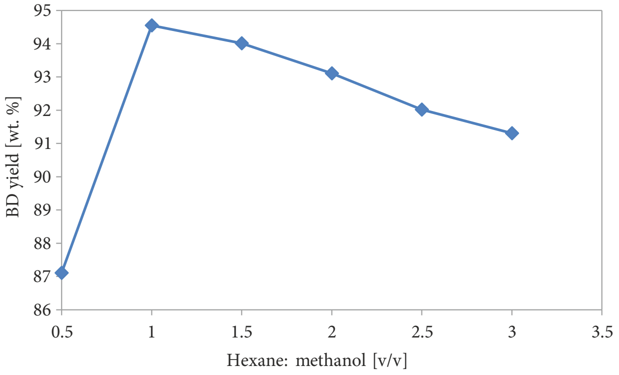

Figure 3. Influence of co-solvent to methanol volume ratio on BAO conversion

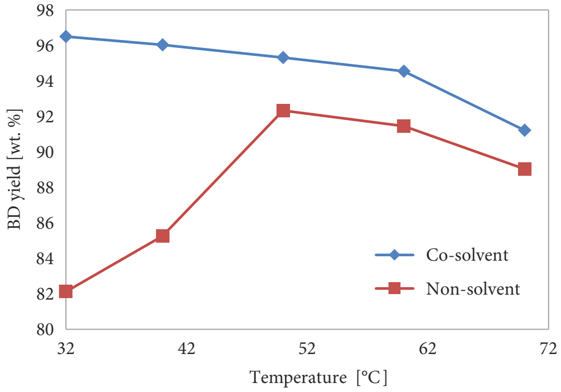

Figure 4. Influence of reaction temperature on BAO conversion

ane to methanol volume ratio, 60 minutes of reaction and 600 rpm rate of stirring. It was observed that co-solvent transesterification of BAO exhibited the highest yield of BD (96.50…95.88% w/w ester content) at the lowest temperature of reaction, i.e. 32 °C, which is far below the boiling point of methanol (68 °C), whereas non-solvent process gave the best yield of BD (92.33…90.12% w/w ester content) at 50 °C. This difference in the optimal reaction temperature between both processes could be attributed to the presence of co-solvent, which decreases the viscosity of the oil and thereby increases the mass transfer between alcohol and the oil, resulting in higher yield of BD. Atapour and Kariminia (2011) investigated transesterification of BAO at various temperatures and found that 50 °C was the optimal which was also in line with results obtained in the present study for non-solvent process. This indicates that reaction temperature is a critical factor in the transesterification of BAO. However, the BD yield decreases at temperatures higher than 32 °C, which could be attributed to the side reaction viz. saponification by the base catalyst at the expense of transesterification. As a result, part of the esters will convert to soap. Thus, the BD yield decreases (Ong *et al.* 2013; Rashid *et al.* 2011). Thus, 32 °C was established as the optimal temperature of reaction.

2.2.5 Influence of the reaction time

The production cost of BD is greatly affected by the reaction time. Consequently, the influence of reaction time on BD yield should be optimized. Different time intervals ranging from (15…90 minutes) were tested during co-solvent and non-solvent transesterification of BAO as seen in Figure 5.

In all experiments, the optimal conditions obtained during the present study were fixed. The results exhibited that yield of BD increased with increasing the reaction time for both processes. However, the conversion of BAO into BD was very rapid and higher in the presence of co-solvent compared to non-solvent process, so that a significant yield of BD (91.50%) was obtained at the first 15 minutes of reaction. Moreover, co-solvent process took shorter time (45 minutes) to produce the highest yield of BD (98.50…97.88% w/w ester content) than non-solvent process, which exhibited the highest of BD (95.44…94.21% w/w ester content) at 60 minutes of reaction. Nevertheless, durations longer than 45 minutes reduced the BD yield due to hydrolysis of some of the formed esters into their free fatty acids and thus the methyl ester yield decreases (Fadhil, Abdulahad 2014; Ong *et al.* 2013).

2.2.6. Influence of co-solvent type

Base-catalysed transesterification of BAO with methanol was also conducted in the presence of various co-solvent including hexane, petroleum ether, acetone, cyclohexane and diethyl ether as shown in Figure 6. These solvents can dissolve the oil in the mixture with methanol to form a homogeneous solution. Furthermore, the addition of high boiling point solvents increases the boiling point of whole solution over boiling point of methanol that enables to carry out the reaction at higher temperature. To investigate the influence of co-solvent type on yield of BD from BAO, other experimental conditions were fixed at 0.60% KOH w/w, 5:1 methanol to lo molar ratio, 1:1 co-solvent to methanol volume ratio, 32 °C reaction temperature, 45 minutes of reaction and a stirring rate of 600 rpm. It was noticed that transesterification of BAO in the presence of any of the tested co-solvents gave a yield up to 90% except acetone. Maximum yield of BD (98.50…97.88% w/w ester content) was obtained with hexane. This may attribute to the fact that hexane dissolves better the oil and thus makes the reaction mixture more homogeneous. As a result, transesterification reaction can proceed more faster. In addition, the boiling point of hexane is closer to that of methanol, which allows its recycling with excess methanol at the same time.

2.2.7. Influence of catalyst type

Different alkali catalysts such as NaOH, CH_3ONa, CH_3CH_2ONa were also investigated during co-solvent transesterification of BAO so as to investigate the influence of the strength of alkalinity of the catalysts on the yield of BD. For 0.60% KOH w/w of oil was the optimal concentration for co-solvent methanolysis of BAO during the present study, similar concentration of above alkaline catalysts were also tested in order to make the results comparable.

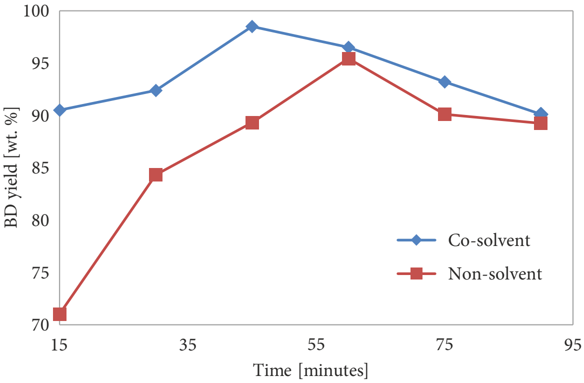

Figure 5. Influence of reaction time on BAO conversion

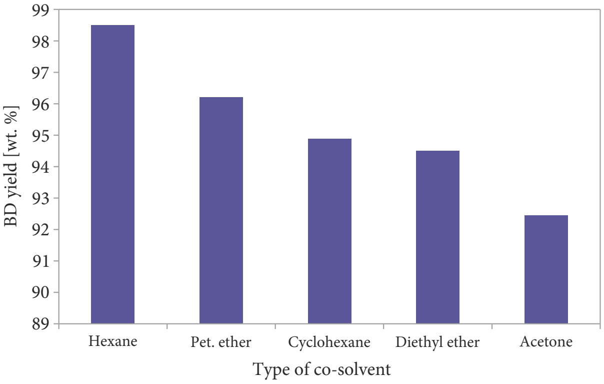

Figure 6. Influence of co-solvent type on BAO conversion

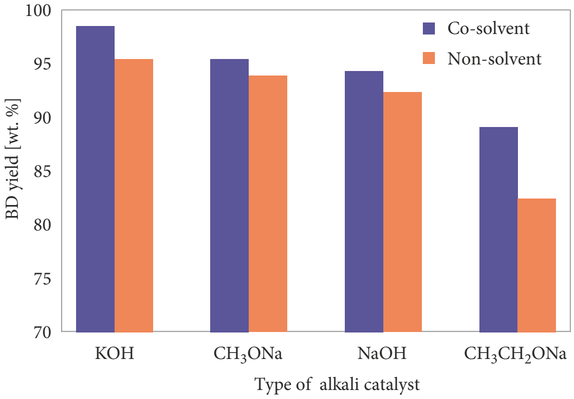

Figure 7. Influence of the alkali catalyst type on BAO conversion

Other variables were fixed at 5:1 methanol to lo molar ratio, 1:1 co-solvent to methanol volume ratio, 32 °C reaction temperature, 45 minutes of reaction and a stirring rate of 600 rpm. As shown in Figure 7, the potassium hydroxide catalyst exhibited the highest yield of BD among other alkaline catalysts. This is due to the higher strength of alkalinity of KOH compared to other alkali catalysts, such that catalyst that is more alkaline is more effective. This statement was further proved by Alhassan *et al.* (2014), Rashid, Anwar (2008) and Fadhil, Ali (2013).

2.2.8. Comparison of results with other published studies

Results of co-solvent methanolysis of BAO were compared with those of other studies. As regard the catalyst concentration, the best concentration of KOH which resulted in maximum yield of BD was 0.60% w/w. Encinar *et al.* (2010) investigated co-solvent methanolysis of rapeseed oil using various concentrations of KOH and found that 0.75% w/w was the optimal concentration, while Luu *et al.*(2014) reported maximum conversion of the esterified *Jatroph curcas seed* oil into BD using 1.0% KOH w/w. Alhassan *et al.*(2014) found that 0.75% w/w of KOH was the best concentration for co-solvent transesterification of cotton seed oil into BD. Co-solvent transesterification of the esterified *jatropha curcas* oil exhibited maximum yield of BD using 0.50% w/w NaOH. The variation in the concentration of the catalyst required to obtain the highest conversion among various feedstocks could be attributed to acidity of the parent oil, type of the utilized base catalyst and type of co-solvent used in the process. It was found that 5:1 was the optimal methanol to oil molar ration during co-solvent transesterification of BAO. Luu *et al.* (2014) and Mohammed-Dabo *et al.* (2012) found that 6:1 and 4:1 were the optimal methanol to oil molar ratios co-solvent transesterification of the Vietnamese esterified *Jatroph curcas* seed oil and *Jatroph curcas* seed oil, respectively. This variation in the optimal methanol to oil molar ratio among different feedstocks may be attributed to the varied nature of the feedstock oils as well as type of co-solvent used. Maximum yield of BD produced form BAO via co-solvent methanolysis was obtained using 1:1 co-solvent to methanol volume ratio. Encinar *et al.* (2010) reported co-solvent transesterification of rapeseed using diethyl ether as a co-solvent and found that 1:1 co-solvent to methanol ratio was the optimal. Mohammed-Dabo *et al.* (2012) investigated co-solvent transesterification of pre-esterified *Jatroph curcas* seed oil and found that 1:1 co-solvent (THF) to methanol was the optimal ratio. The variation in the optimal ratio of co-solvent compared to other studies could be attributed to type of co-solvent utilized during the process. Co-solvent transesterification of BAO with methanol resulted in maximum yield of BD when the process was conducted at 32 °C. Encinar *et al.* (2010) found that 30 °C was the optimal temperature for co-solvent methanolysis of rapeseed, whereas Mohammed-Dabo *et al.* (2012) and Luu *et al.* (2014) found that 40 °C was the optimal temperature to produce maximum yield of BD from the esterified *Jatropha curcas* oil via co-solvent process. Chemical composition of the feedstock oils could be the main reason for this variation in the optimal temperature required for maximum conversion among various feedstock oils. The best yield of BD produced from BAO via co-solvent transesterification was obtained after 45 minutes of reaction. Alhassan *et al.* (2014) mentioned that co-solvent transesterification of cotton seed oil required 45 minutes of the reaction to yid the highest conversion, whereas co-solvent methanolysis of rapeseed oil took 60 minutes of the reaction to reach maximum conversion. Mohammed-Dabo *et al.* (2012) investigated co-solvent transesterification of pre-esterified *Jatroph curcas* seed oil at various durations and found that a duration of 50 minutes was the optimal, whereas Luu *et al.* (2014) found that the optimal reaction time for transesterification of the esterified *Jatropha curcas* oil was 60 minutes. Regarding type of co-solvent utilized during transesterification, it was noticed that hexane was the optimal co-solvent used for transesterification of BAO with methanol compared to other co-solvents. Encinar *et al.* (2010) tested various co-solvents on methanolysis of rapeseed oil and found that diethyl ether and *t*-butyl methyl ethyl ether were the best co-solvents due to they gave the highest yield of BD compared to others. Luu *et al.* (2014) reported that acetonitrile was the best co-solvent on methnolysis of the esterified Vietnamese *Jatropha curcas* oil, whereas Mohammed-Dabo *et al.* (2012) reported maximum yield of BD from the esterified *Jatropha curcas* oil using THF as a co-solvent.

2.3. Fuel properties evaluation

The physical and chemical properties of BD produced from BAO via co-solvent transesterification were determined in accordance with ASTM standards and listed in Table 3. For comparison, properties of BD prepared via non-solvent transesterification were determined as well.

The density of the prepared BD is 0.8787 g/mL, which is lower than densities of *Thespesia populnea L.* seed oil methyl ester (TPOME) and sunflower oil seed methyl ester (SOME) which values were 0.8800 g/mL (Rashid *et al.*

Table 3. Properties of BD produced from BAO compared to the standard BD and other BDs

Property	BD	BD*	ASTM D6751-15ce1	PD	SOBD[a]	TPOBD[b]
Yield [wt.%]	98.50±0.54	95.44	–	–	97.10	–
Ester content [% w/w]	97.88±0.32	93.98	96.50	–	–	–
Density @ 15.6 [g/ml]	0.8787±0.0010	0.8801	0.9000	0.8300	0.8800	0.8800
Kinematic viscosity @ 40 °C [mm^2/s]	4.09±0.22	4.48	5.0	2.04	4.90	4.25
Flash point [°C]	165±1.0	175	130	77.0	170.0	176.0
Acid value [mg KOH/g oil]	0.08±0.01	0.12	0.50	0.40	0.24	0.25
Saponification value [mg KOH/g oil]	188.12±1.20	186.24	–	–	–	–
Iodine value [100 mg I_2/g oil]	93.04±1.50	92.55	120.0	8.0	–	–
Cloud point [°C]	2.0±0.50	4.0	–	8.0	1.0	8.0
Pour point [°C]	–4.0±0.50	–2.0	–	–16.0	–4.0	9.0
Conradson carbon residue [%]	0.029±0.001	0.032	0.05	0.20	–	–
Refractive index @ 20 °C	1.4550±0.0002	1.4553	–	1.4780	–	–
Total glycerol [wt. %]	0.1002±0.0011	0.1101	0.24	–	0.20	0.11
Soap [ppm]	0.2403±0.0023	0.4004	–	–	–	–
Cetane number	44.22±1.0	44.45	–	–	–	59.80

Notes: *BD produced via non-solvent process; [a]Sunflower oil seed methyl ester (SOME) from Rashid *et al.* (2009); [b]*Thespesia populnea L.* seed oil methyl ester (TPOME) from Rashid *et al.*(2011).

2009; Rashid *et al.* 2011). The kinematic viscosity offered by the prepared BD is 4.09 mm^2/s, which is lower than viscosities of TPOME and SOME (Rashid *et al.* 2009; Rashid *et al.* 2011). BD from BAO exhibited lower acid value (0.08 mg KOH/g) than the acid values of TPOME and SOME (Rashid *et al.* 2009; Rashid *et al.* 2011). The flash point offered by the prepared BD is 165 °C compared to 170 and 176 C for SOME and TOPME, respectively (Rashid *et al.* 2009; Rashid *et al.* 2011). The higher flash point of BD compared to conventional diesel rendering it safer for transportation purposes. The refractive index of BD from BAO is 1.4509 compared to 1.4720 for its respective parent oil. This finding assures the conversion of oil to its corresponding ester. The flow properties of BD can be determined in terms of the cloud and pour points, which values were 2 and –4 °C, respectively. The cloud and pour points of the prepared BD were much better than those reported for SOME and TPOME (Rashid *et al.* 2009; Rashid *et al.* 2011). This variation could be attributed to the high level of unsaturated ted fatty acids of BAO methyl ester compared to SOME and TPOME. Although the cloud and pour points of BD are higher than those observed for PD, BD from BAO is suitable for use in cold weather conditions prevailing in northern Iraq in winter. The content of unsaturated fatty acids of BD can be described by the iodine value. The iodine value of the produced BD is 93.04 mg I_2/100 g. The Conradson carbon residue was used to determine the carbon residue of BD. It was found that the Conradson carbon residue value of BD from BAO satisfied the limits prescribed by ASTM D6751-15ce1 (<0.05 max.) as shown in Table 3. The degree of completion of the transesterification process and the effectiveness of the purification process applied can be measured as a function of the amount of free and total glycerine found in the BD after purification (Manique *et al.* 2012). It was found that the produced BD contains lower amount of glycerine (0.1002 wt. %) than TPOME and SOME. This reflects the high purity level of the produced BD. The cetane number offered by BD from BAO is 44.22 compared to 59.8 for TPOME (Rashid *et al.* 2009). The low cetane number of the prepared BD compared to that of TPOME is attributed to the high level of saturated fatty acids in TPOME compared to BAO methyl ester. It can also be seen from Table 3 that the yield and ester content of BD produced via co-solvent transesterification were higher than those observed for that produced through non-solvent process. Moreover, the fuel properties of BD produced via co-solvent transesterification were better than those of BD prepared via non-solvent transesterification. This could be attributed to the high ester content of the former compared to the latter.

Encinar *et al.* (2007) reported that BD of higher ester content has better properties than those of lower esters content. Our findings were in line with those reported by Encinar *et al.* (2007). As the fuel properties of the prepared BD met the required limits as specified by the ASTM D6751-15ce1 for BD; BD developed from BAO can be used as fuel in the internal combustion engines without any modification in the engine.

2.4. Analysis of BD from BAO

BD produced from BAO through co-solvent transesterification was analysed by using TLC and FTIR spectroscopy. The TLC photograph which is depicted in Figure 8 shows that the parent oil showed three spots at various rate of flow (R_f = 0.07, 0.29 and 0.58 cm). These spots indicate the fractionation of BAO into mono-, di- or tri- glycerides as well as free fatty acids. On the other hand, the BD was free of any impurities such as mono, di- or tri glycerides as well as free fatty acids, such that it showed one spot at various rate of flow (R_f = 0.76 cm). This spot assures the entire conversion of the oil to its corresponding esters (Fadhil, Ali 2013; Fadhil *et al.* 2014). The observed bands in the parent oil were as follows: The absorption band at 2854…3008 cm^{-1} refers to asymmetric and symmetric CH_3 stretching vibrations (–CO–O–CH_3), whereas that observed at 1437…1464 cm^{-1} indicates the –C–H (alkane) bonding.

The absorption band at 1099…1242 cm^{-1} attributes to stretching vibration of the (–C–O–) ester groups, whilst that observed at 1655 cm^{-1} indicates (C=C) the stretching modes characteristic of olefins. The characteristic absorption band at 1747 cm^{-1} refers to the ester carbonyl group (C=O). The main differences observed between the FTIR spectra of BAO and its BD are a small displacement of the stretching C=O band and the stretching C–H band as well as the bending band of C–H of the BD to lower energy (Figure 9). This is attributed to the substitution of the glycerol by the methoxilic radical. Another piece of evidence on the conversion of the oil to its corresponding ester is that the area under the absorption bands of the stretching C=O band and stretching C–H band as well as the C–H bonding band of the methyl esters are much lower than their corresponding in the original oil. Thus, the results indicate that the transesterification process is a successful means to alter the fuel properties of oil and transfer it into a more valuable fuel (Fadhil, Ali 2013).

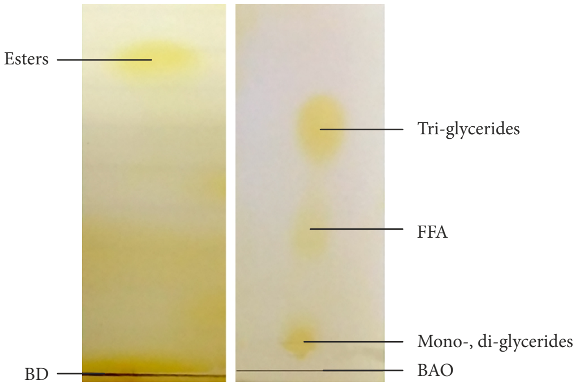

Figure 8. The TLC photographs of BAO and its optimal BD sample

2.5. Properties evaluation of BD and PD blends

BD and PD can be blended with each other at all ratios because they are miscible. Furthermore, BD has some characteristics, which are not found in PD, and vice versa. Thus, their blending will enhance properties of each other.

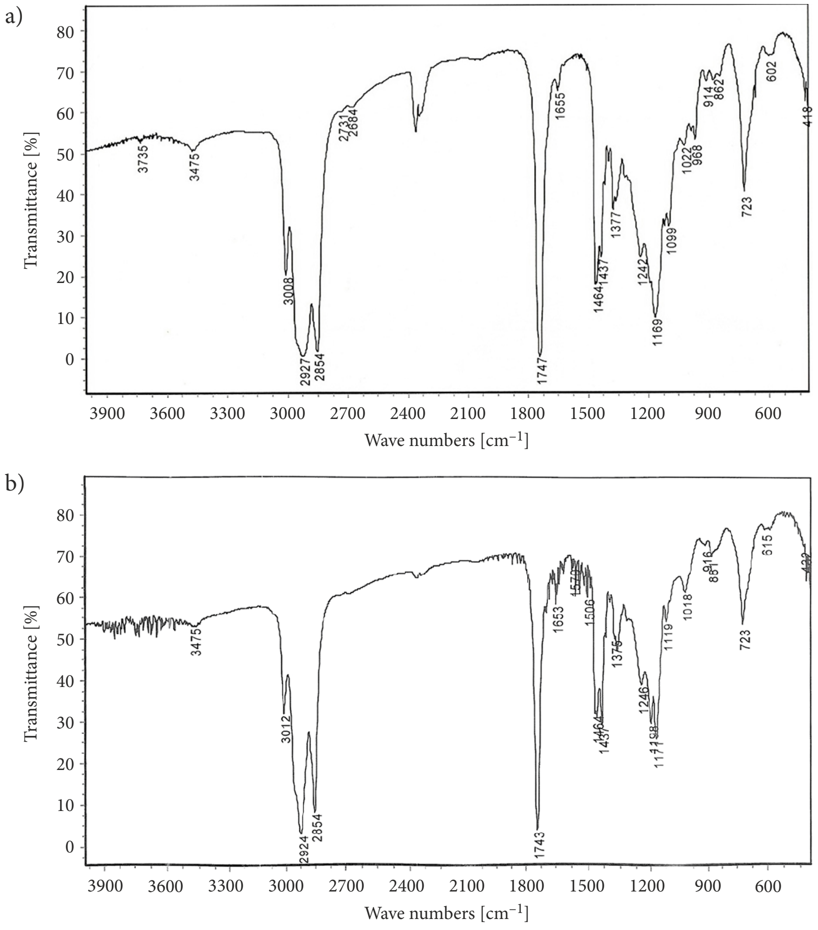

Figure 9. The FTIR spectra of BAO (a) and its optimal BD (b) samples

Table 4. Properties of (BD + PD) blends

Sample	Density @ 15.6 °C [g/ml]	Kinematic viscosity @ 40 °C [mm^2/s]	Flash point [°C]	Pour point [°C]	Acid value [mg KOH/g]	Refractive index @ 20 °C
PD	0.8300	2.17	76.0	–16.0	0.46	1.4780
B_{100}	0.8787	4.09	165.0	–4.0	0.08	1.4533
B_{10}	0.8422	2.89	78.0	–16.0	0.37	1.4721
B_{20}	0.8513	3.22	81.0	–14.0	0.32	1.4656
B_{30}	0.8545	3.78	86.0	–13.0	0.31	1.4621
B_{40}	0.8658	3.90	89.0	–12.0	0.28	1.4591
B_{50}	0.8701	3.96	93.0	–11.0	0.24	1.4557

In the present study, various blends of BD and PD (B_{10}, B_{20}, B_{30}, B_{40} and B_{50}) were prepared and assessed for several interesting properties such as the density, kinematic viscosity, pour point, flash point, acid value and refractive index as given in Table 4.

The density of PD increased markedly with the increment of BD content in the blends. The density values of the blends ranged from 0.8422 to 0.8701 g/mL. However, the value remained within the limits prescribed by the ASTM D7467-17 standards. The viscosity of PD was also increased with increasing BD content in the blends. The viscosity values of the blends ranged from 2.89 to 3.96 mm^2/s. The increment in viscosity of PD is due to the high viscosity of BD compared to PD. However, kinematic viscosities were satisfactory according to (PD + BD) blend ASTM D7467-17 standards. The flash point of PD is 76 °C compared to 165 °C for BD. The flash point of BD is about double the value of that for PD. Thus, it represents an important safety asset for BD. As in the case of viscosity, the flash point of PD increased with increasing BD content in the blend. The flash point values of the blends ranged from 78.0 to 93.0 °C. The advantages of blending BD with PD are to make the latter possible to store and safer to handle for transportation sector (Silitonga *et al.* 2013a, 2013b). One of the disadvantages of BD is its high flow properties such as pour point. This property is connected greatly to fatty acid composition of BD. Results in Table 4 display that the pour point of PD increases with the increment of BD content in the blends. This may be due to the high pour point of BD compared to PD. However, the pour point of PD remained low and suitable for use in some cold weathers such as those prevailing in north Iraq in winter. High values of the density, viscosity and flash point of BD compared to PD is due to the high molecular mass of BD compared to the conventional diesel fuel (Candeia *et al.* 2009; Fadhil *et al.* 2014). On the other hand, the acid value and refractive index of PD are higher than those of BD. This could be attributed to the presence of some aromatic fractions in PD. However, blending of PD with BD results in a reduction in the acid value and refractive index of the former. These findings were further proved in our previous studies (Fadhil, Ali 2013; Fadhil *et al.* 2014) as well as by several researchers (Candeia *et al.* 2009; Silitonga *et al.* 2013a, 2013b; Sánchez *et al.* 2015).

2.6. Distillation curves

The boiling point of a liquid fuel is affected by the composition of the fuel and thus affects greatly the combustion characteristics of diesel engines. The distillation curve provides important information about the composition of the fuel. The high distillation temperature of a liquid fuel results in shorter ignition delay and decreases the probability of the occurrence of knocking in diesel engines (Abd Rabu *et al.* 2013; Fadhil, Ali 2013; Fadhil *et al.* 2014; Lin, Li 2009). The distillation curve of BD, PD and B_{50} is illustrated in Figure 10.

It is obvious from the Figure 10 that the initial boiling point (IBP) of PD is lower than those observed for BD and B_{50} samples. This means that PD is more volatile than BD and B_{50} samples. This is due to that PD consists of hundreds of different compounds of different boiling points, whereas BD consists mainly of straight chain hydrocarbons with 16…20 carbon atoms that have also adjacent boiling points. Moreover, T_{90}, which is the temperature at which 90% of the fuel is distilled was higher in BD and B_{50} than PD. It is 345 °C for BD compared to 320 °C for PD. This could be attributed to the high molecular mass of BD compared to PD (Abd Rabu *et al.* 2013; Fadhil, Ali 2013; Fadhil *et al.* 2014; Lin, Li 2009). In comparison to other BDs from the literature, it was found that the trend of the curve of the distillation temperatures of BD was similar and in agreement with those observed for other BDs from the literature (Abd Rabu *et al.* 2013; Lin, Li 2009).

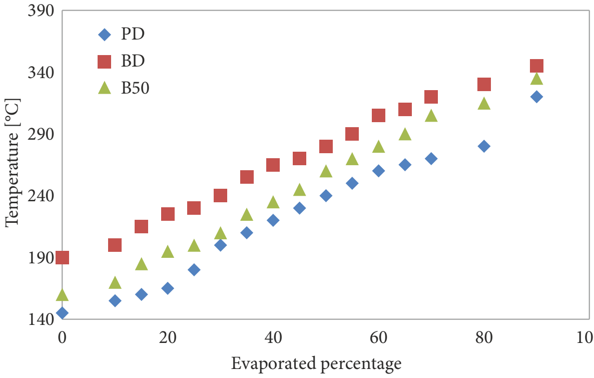

Figure 10. The distillation curves of PD, BD and B_{50} samples

Conclusions

The presence of co-solvent can facilitate transesterification reaction. The utilization of co-solvent produces high yield of BD in shorter reaction time and lower temperature compared to non-solvent process.

Among tested co-solvents, hexane was the most effective one and 1:1 hexane to methanol volume ratio was the optimal for assuring the highest conversion.

KOH was the best catalyst for co-solvent methanolysis of BAO compared to other base catalysts. The highest conversion of BAO into BD (98.50 wt. % with an ester content of 97.88 wt. %) was achieved at 0.60 wt. % KOH, 5:1 methanol to oil molar ratio, 1:1 hexane to methanol volume ratio, 32 °C reaction temperature, 45 minutes of reaction and a stirring rate of 600 rpm.

In comparison to other studies, implying of co-solvent within the reaction medium was very effective in reduction the amount of the catalyst, methanol to oil molar ratio, temperature and time required for maximum conversion which means lower cost of production.

The properties of BD fuel produced through co-solvent process were superior, than those produced via non-solvent and within the requirements of ASTM D6751-15ce1 BD suggesting its suitability as a fuel for diesel engines.

Furthermore, the fuel properties of (BD + PD) blends met the requirements prescribed by the ASTM D7467-17 standards.

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