



ORIGINAL ARTICLE

# *Silybum marianum* L. seed oil: A novel feedstock for biodiesel production



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Received 27 June 2012; accepted 5 November 2012

Available online 23 November 2012

## KEYWORDS

*Silybum marianum* L. seed oil;  
Two-step transesterification;  
Acid–base transesterification;  
Biodiesel;  
Fuel properties

**Abstract** In the present study, biodiesel was produced from a novel non edible oil source, *Silybum marianum* L. seeds oil (SMSO). The acid value of the extracted oil was found to be 13.60 mg KOH/g. Therefore, a dual step process viz. acid–base catalyzed transesterification was developed to produce the biodiesel. Free fatty acids in SMSO were converted into methyl esters through the esterification of the oil by using hydrochloric acid (HCl) as an acid catalyst with 6:1 methanol to molar ratio at 60°C for 1 h, to reduce the acid value of the parent oil to below (2 mg KOH/g of oil), a value safe to produce the biodiesel through alkaline catalyzed transesterification. During alkaline-catalyzed transesterification, the parameters of this step such as alkaline catalyst type and concentration, methanol to oil molar ratio, reaction temperature and reaction duration were optimized. The results of esterification indicated that 1.0% HCl w/w of oil was optimal for the esterification, because it lowers the acid value to the minimum. For alkaline transesterification, a maximum conversion of (95.0%) was obtained by using potassium hydroxide as a catalyst with a concentration of 0.90% w/w of oil, 6:1 methanol to oil molar ratio, 60 °C reaction temperature and a reaction duration of 100 min. Biodiesel was also analyzed by using thin layer chromatography and Fourier transform infra red spectroscopy. The properties of the produced biodiesel are found to conform with the ASTM standard specifications.

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## 1. Introduction

Fossil fuels such as petroleum, coal and natural gas are the main sources of energy. However, the increasing reliance of mankind on fossil fuels increased the depletion rate of resources and global warming threats. As a result, alternative fuels must be found to reduce the reliance on fossil sources and to reduce greenhouse gas emissions as well. Biomass derived fuels could be one of the solutions, because they are renewable and act as a carbon sink (Alamu et al., 2008; Bati-dzirai et al., 2006; Knothe and Steidley, 2005; Moghaddam et al., 2010).

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Biodiesel is one of the liquid biofuels that is gaining increasing attention as an alternative fuel to petro diesel. It can be produced from animal fats or vegetable oils through the transesterification process. In this process, the oil or fat is reacted with alcohol (methanol or ethanol) in the presence of alkaline, acid or enzyme catalysts to produce mono alkyl ester (biodiesel) and glycerin as side products (Mathiyazhagan et al., 2011; Chung et al., 2009; Alptekin and Canakci, 2010; Malaya et al., 2005; Bhatti et al., 2008; El-Mashad et al., 2008; Fadhil et al., 2012). However, the use of vegetable oils as a source for biodiesel production competes with its use as a source of food. Therefore, cheap resources must be used as raw materials for producing biodiesel. Animal fats, waste frying oils and non-edible oils seem suitable raw materials to produce biodiesel (Bhatti et al., 2008; El-Mashad et al., 2008; Hawash et al., 2009; Cankci and Sanli, 2008). However, most of these resources are of high free fatty acid content (FFA) which require a two-step transesterification (El-Mashad et al., 2008; Alptekin and Canakci, 2010; Cankci and Sanli, 2008). It is well known that oils of high FFA content are not suitable for alkaline-catalyzed transesterification, unless their FFA content is reduced to (<1%), which corresponds to 2 mg KOH/g oil, because they consume the alkaline catalyst in the form of soaps; hence reducing the biodiesel yield. As a result, a dual-step transesterification namely acid–base catalyzed transesterification is recommended for such raw sources (El-Mashad et al., 2008; Cankci and Sanli, 2008; Ramadhas et al., 2005). In this process, the oil with high FFA content is treated with methanol in the presence of an acid catalyst to reduce its FFA content to the safe limits, and then the resultant oil is converted into biodiesel using an alkaline catalyst.

*Silybum marianum* L. is a wild annual plant. It belongs to the Asteraceae family. It grows naturally at mild climatic regions of Iraq. The seeds of this plant are used as a source of many flavone compounds. The oil extracted from these seeds can be used as a cure for many diseases including Viral Hepatitis and Cirrhosis. To the best of our knowledge, no literature was reported about the production of biodiesel from this feedstock.

The present study aims to produce biodiesel from an ideal novel feedstock namely *S. marianum* L. seed oil through acid–base catalyzed transesterification (ABCT). The oil is esterified with methanol in the presence of hydrochloric acid as a catalyst. Then, the resultant oil is converted into biodiesel through alkaline-catalyzed transesterification. The influence of the catalyst type and concentration, methanol to oil molar ratio, the reaction temperature and the reaction duration on the alkaline-catalyzed transesterification were investigated. The fuel properties of the produced biodiesel are determined in accordance with the ASTM standard.

## 2. Experimental

### 2.1. Feedstock preparation

*Silybum marianum* L. seeds were harvested from lands extending within the Mosul University, north of Iraq during the summer of 2011. The kernels were stripped from the shells, and dried in an oven at 50°C for 5 h. Then, the dried kernels were crushed using a coffee grinder, and fed to a Soxhlet extractor connected with a 1 L round bottomed flask. The extraction

was carried out using *n*-hexane as a solvent. After 10 h of extraction, the solvent was recovered by distillation under vacuum using a rotary evaporator. The oil was mixed with freshly activated sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) to eliminate the residual moisture. Finally, the oil was filtered, transferred into a sealed container, and was kept at 5°C for further assessment and use. Mean molecular weight (MMW) of the oil was determined according to Zhu et al. (2006).

$$\text{MMW} = \frac{56.1 \times 1000 \times 3}{(\text{SV} - \text{AV})}$$

where SV is the saponification value and AV is the acid value.

### 2.2. Chemicals

Methanol (99.90%), potassium hydroxide, sodium hydroxide, sodium methoxide, sodium ethoxide (99.90%) and calcium chloride were supplied by Merck, while chloroform, *n*-hexane and hydrochloric acid were supplied by Fluka. All the chemicals were of analytical grade and used as received without any further purification.

### 2.3. Biodiesel production from SMSO

The acid value of SMSO was found to be 13.60 mg KOH/g oil, which corresponds to 6.80% of FFA content. This value is much higher than the safe limits for alkaline-catalyzed transesterification. As a result, a dual-step transesterification is required to produce the biodiesel (BD) from SMSO. Acid–base catalyzed transesterification (ABCT) was used by many investigators to produce BD from oils of high FFA content (El-Mashad et al., 2008; Cankci and Sanli, 2008; Ramadhas et al., 2005). Hence, SMSO was converted into BD through a two-step transesterification, namely ABCT.

#### 2.3.1. Acid esterification of SMSO

The raw oil of *S. marianum* L. seeds (50 g) was poured into a glass reactor (a 2 L three necked round bottomed flask) equipped with a magnetic stirrer, a cooling system to prevent alcohol loss and a controlled heating system. The oil is preheated to 60°C to eliminate any moisture in the oil, then the catalyst solution (a specified amount of HCl% w/w of oil dissolved in methanol at a molar ratio of 6:1 methanol to oil) was poured into the reactor. The mixture was heated with simultaneous stirring at (600 rpm) for 1 h at 60°C. After an hour of the reaction, the products were transferred into a separating funnel for phase separation. Two phases were obtained, the lower phase contains water, while upper phase contains the unreacted methanol and the produced esters. The ester layer was washed by warm distilled water (DW), and then passed over Na<sub>2</sub>SO<sub>4</sub> to remove the residual moisture. After the acid esterification, properties of the resultant oil including the acid value, viscosity, density, saponification value, flash point, pour point, refractive index and carbon residue were determined according to the ASTM standard.

#### 2.3.2. Base catalyzed transesterification

After acid esterification, the acid value of the raw oil was reduced to 1.89 mg KOH/g oil, a value optimal to produce BD through alkaline-catalyzed transesterification (ACTE). The oil was poured into a glass reactor (a three-necked round bottomed flask) equipped with a cooling system to prevent alcohol

loss and a controlled heating system. The oil was pre-heated to 60°C, and then the catalyst solution (alkaline catalyst% w/w of oil) dissolved in methanol at a molar ratio of 6:1 methanol to oil was added to the oil. The mixture was heated with simultaneous stirring at 600 rpm for 1 h at 60°C. After the reaction was over, the products were transferred to a separating funnel to obtain two layers. The upper layer contains crude BD, while the lower contains glycerol and other impurities. The glycerol layer was withdrawn and discarded, whereas the crude BD was washed by warm distilled water (3 × 25 mL), and then passed over Na<sub>2</sub>SO<sub>4</sub> to remove the residual moisture. Finally the yield of the produced BD was determined as follows (Rashed and Anwar, 2008a,b; Fadhil et al., 2012):

$$\text{Yield\%} = \frac{\text{Wt of the refined methyl esters}}{\text{Wt of oil used}} \times 100$$

#### 2.4. Properties evaluation of biodiesel

The properties of the produced biodiesel fuel were determined in accordance to the ASTM standards. Iodine Number (IN) was measured according to the Hanus method. Higher Heating Value (HHV) was determined depending on equations proposed by Demirbas (2008). The cetane indices of the the oil and the produced biodiesel were calculated by using following formula (Willard, 1997):

$$\text{CI} = -420 : 34 + 0 : 016G^2 + 0.192G(\log T_{50}) + 65.01(\log T_{50})^2 - 0 : 0001809T_{50}^2$$

where  $G$  is the API (American Petroleum Institute) specific gravity and  $T_{50}$  is the distillation temperature at which 50 vol.% of fuel sample was distilled and condensed in a unit of °F(20).

#### 2.5. Analysis of biodiesel by using thin layer chromatography

The produced BD was analyzed by using thin layer chromatography (TLC). Silica gel plates (3 × 10 cm glass) were washed by methanol, and activated in an oven for 2 h at 110°C. Then, the oil or BD was dissolved in *n*-hexane. Later on, it was spotted on the TLC plates with a capillary tube. The plates were developed (eluted) with hexane/di ethyl ether/acetic acid (80:20:1, vol/vol/vol). After the fractionation, the solvent was evaporated and the spots on the TLC plate were visualized by iodine vapor (Hawash et al., 2009).

#### 2.6. FTIR analysis of biodiesel

The Fourier transform infra red (FTIR) spectra of SMSO and its BD sample were determined by using the FTIR spectrophotometer. The KBr cell was used for this purpose. The FTIR spectrum was measured within a range of 400–4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution.

### 3. Results and discussions

#### 3.1. Feedstock properties

The present study investigates the use of SMSO as a potential feedstock for BD production. The fatty acid composition and the physical and chemical properties of SMSO are given in

**Table 1** Fatty acid profile of SMSO.

Fatty acid (wt)%	SMSO	Rubber seed oil <sup>a</sup>	Mahua oil <sup>b</sup>	Polanga seed oil <sup>c</sup>
C <sub>16</sub>	9.40	10.20	16–28	12.01
C <sub>18</sub>	6.60	8.70	20–25.1	12.95
C <sub>18:1</sub>	20.80	24.60	41.0–51.0	34.09
C <sub>18:2</sub>	53.30	36.90	8.9–13.70	38.26
C <sub>18:3</sub>	Trace	16.30	4.80	–
C <sub>20</sub>	3.80	–	–	–

<sup>a</sup> Ramadhas et al. (2005).

<sup>b</sup> Ghadge and Raheman (2006).

<sup>c</sup> Sahoo et al. (2007).

Table 1. It was found that SMSO has high unsaturated fatty acid content which constitutes (73.0%) of the total fatty acids. Linoleic acid content was (53.30) of the total composition followed by oleic acid (20.80%) (El-Mallah et al., 2003). However, SMSO has higher unsaturated fatty acid content compared to some vegetable oils as can be seen in Table 1. Major physico-chemical properties of SMSO were determined and are listed in Table 2. Each value was measured in triplicate, and the mean was recorded. The oil content of SMSO ranged between 28% and 30% on a dry weight basis, which is higher than that reported for several oil seeds such as soybean and cottonseeds which have an oil content of 20% and 14%, respectively. The mean molecular weight of SMSO was 895 g/mole. This value is close to those reported for some vegetable oils like olive oil = 857 and sunflower oil = 876 g/mole (George et al., 2009). Pour point and iodine number of SMSO were –8 and 99, respectively. This reflects the presence of high unsaturated fatty acid content in SMSO. The kinematic viscosity of crude SMSO was 42.0 mm<sup>2</sup> s<sup>-1</sup>, whereas the density was 0.9041 g/ml. The saponification value of SMSO was 204 mg KOH/g oil.

#### 3.2. Biodiesel preparation from SMSO

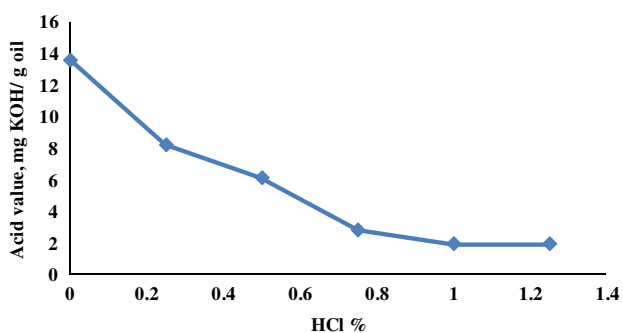
*S. marianum* L. seed oil was used as a novel feedstock to produce BD. The FFA content of SMSO was found to be 6.80%. This value is higher than the safe limits for alkaline catalyzed transesterification. High FFA content in the oil or fat results in soap formation when the alkaline-transesterification is applied; because part of the alkali catalyst is consumed in neutralizing the FFA in the feedstock. As a result, the yield of BD decreases. Besides, the separation of the produced methyl esters from the glycerol fractions becomes more complicated (El-Mashad et al., 2008; Koria and Thangaraj, 2010). Consequently a dual-step transesterification viz. acid–base transesterification was used to produce BD from SMSO as will be seen later.

##### 3.2.1. Acid esterification

The purpose of this step was to reduce the FFA content in SMSO. Thus, the raw oil was esterified by using various concentrations of HCl (0.25–1.25% w/w of oil with 0.25% increments) with a 6:1 methanol to oil molar ratio, while other experimental parameters were kept fixed (temperature of 60°C, stirring rate of 600 rpm and a duration of 1 h). Fig. 1 shows that the acid value of SMSO reduces with the increment of HCl concentration. The lowest acid value was obtained by using 1.0% w/w HCl. Therefore, this concentration was re-

**Table 2** Properties of SMSO and some vegetable oils.

Property	SMSO	Rubber seed oil <sup>a</sup>	Mahua oil <sup>b</sup>	Polanga ( <i>Calophyllum inophyllum</i> ) <sup>c</sup>
Density @ 16	0.9141	0.91	0.960	0.896
Kinematic viscosity @ 40 °C	42.0	66.20	24.58	71.98
Flash point °C	230	198	NA	221
Acid value mg KOH/g oil	13.60	34.0	38.0	44
Saponification value mg KOH/g oil	195	–	–	–
Iodine number mg I <sub>2</sub> /100 oil	99	–	–	–
Cloud point °C	–2	–	–	–
Pour point °C	–8	–	–	–
Conradson carbon residue	0.15	–	–	–
Refractive index @ 20 °C	1.470	–	–	–
Cetane number	34.04	–	–	–
Higher heating value MJ/kg	39.35	37.50	–	39.25
Mean molecular weight g/mole	857	–	–	–

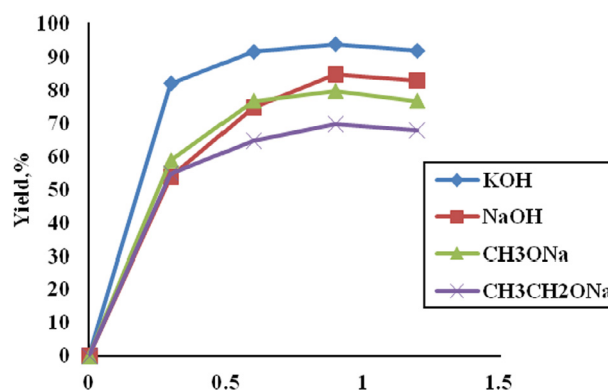
<sup>a</sup> Ramadhas et al. (2005).<sup>b</sup> Ghadge and Raheman (2006).<sup>c</sup> Sahoo et al. (2007).**Figure 1** Influence of HCl concentration on the acid value of SMSO.

garded to be optimal and used to prepare the feedstock for the alkaline-transesterification.

### 3.2.2. Base transesterification

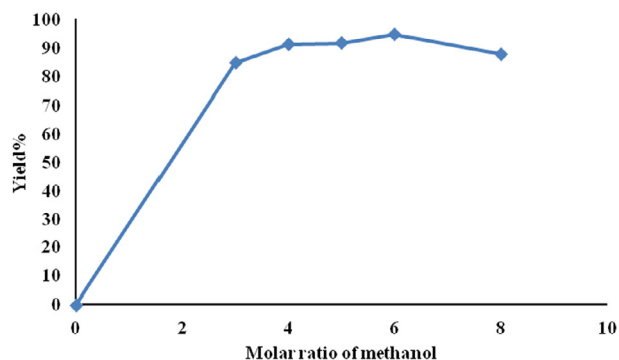
After reducing the acid value of SMSO to 1.89 mg KOH/g, the resultant oil was converted into BD fuel through ACTE. The influence of the catalyst type and concentration, molar ratio of methanol, reaction temperature and reaction duration on the yield of the produced methyl esters was investigated.

**3.2.2.1. Influence of the catalyst type and concentration.** The influence of the catalyst type on the transesterification of SMSO was investigated using different alkaline catalysts (KOH, NaOH, CH<sub>3</sub>ONa and CH<sub>3</sub>CH<sub>2</sub>ONa). Various concentrations of the alkaline catalyst ranging from 0.30% to 1.20% w/w of oil with 0.30% increments were tried. In all experiments 6:1 methanol to oil molar ratio, reaction temperature of 60°C, reaction duration of 60 min and stirring rate of 600 rpm were chosen. The results in Fig. 2 show that the highest yield of BD was obtained by using a concentration of 0.90% w/w of oil for all of the used catalysts. Beyond this concentration, a reduction in the BD yield was observed. This is because higher concentration of the catalyst causes soap formation, which in turn prevents the separation of BD from glycerin fractions. As a result, the BD yield decreases (Koria and Thangaraj,

**Figure 2** Influence of the catalyst type and concentration on the biodiesel yield.

2010). Among the tested catalysts, potassium hydroxide (KOH) exhibited the highest yield of methyl esters (94.0%). Meher et al. (2006) and Doradoa et al. (2006) reported similar findings during the transesterification of *Brassica carinata* and *Pongamia pinnata* oils with methanol. Thus, the KOH was chosen as the best catalyst, and a concentration of a 0.90% w/w of oil was considered to be optimal, and hence used to investigate the influence of the other parameters.

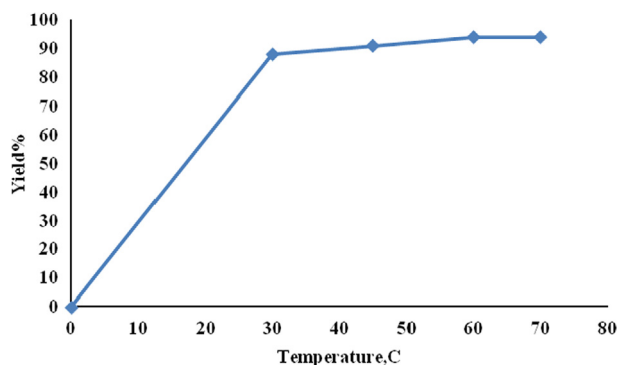
**3.2.2.2. Influence of methanol to oil molar ratio.** One of the parameters affecting the yield of BD is the alcohol to oil molar ratio. It is well known that 3:1 molar ratio of methanol is sufficient to derive the TE reaction. However, as the transesterification process is a reversible reaction; a higher molar ratio of methanol is required to shift the reaction toward the products side and to produce more methyl esters (Ramadhas et al., 2005; Koria and Thangaraj, 2010). To investigate the influence of methanol molar ratio on the BD yield, various methanol to oil molar ratios (3:1, 4:1, 5:1, 6:1, 8:1) were tried. In all experiments, 0.90% KOH w/w of oil, 60°C reaction temperature, 60 min reaction duration and a stirring rate of 600 rpm were employed. Fig. 3 shows that the yield of BD increases with the increment of molar ratio of methanol. The highest BD yield (94%) was obtained at a 6:1 methanol to oil molar ratio.



**Figure 3** Influence of the molar ratio of methanol on the biodiesel yield.

Nevertheless, molar ratios of methanol higher than 6:1 result in a lower BD yield, because it makes the separation of glycerin difficult due to the increment of glycerol solubility in methanol. Besides, when the glycerol is found in the solution, it shifts the equilibrium to the reactants side, reducing the BD yield (Koria and Thangaraj, 2010). Rashid et al. (2008a,b) reported the optimal conversion of sunflower oil to methyl esters with a 6:1 methanol to oil molar ratio. Similar findings were also reported by Ramadhas et al. (2005). Therefore, a 6:1 methanol to oil molar ratio was regarded to be optimal and used to investigate the influence of other parameters.

**3.2.2.3. Influence of reaction temperature.** The influence of reaction temperature on the BD yield was investigated through performing the transesterification at various temperatures (32, 45, 60 and 70°C). In all the experiments 0.90% KOH w/w of oil, 6:1 methanol to oil molar ratio, 60 min reaction duration, and a stirring rate of 600 rpm were chosen. Fig. 4 shows that the BD yield increases with the increment of the reaction temperature. This is for the rate of TE rise with increasing of temperature (Ramadhas et al., 2005). The highest BD yield (94%) was obtained at 60°C reaction temperature. However, no increase in the BD yield was observed with a further increase in the reaction temperature. Moreover, temperature higher than 60°C must be avoided because it darkens the product (Ramadhas et al., 2005). Furthermore, higher temperature adds an extra cost of production. Therefore, a temperature of 60°C was regarded to be optimal and hence used to investigate the influence of other parameters.

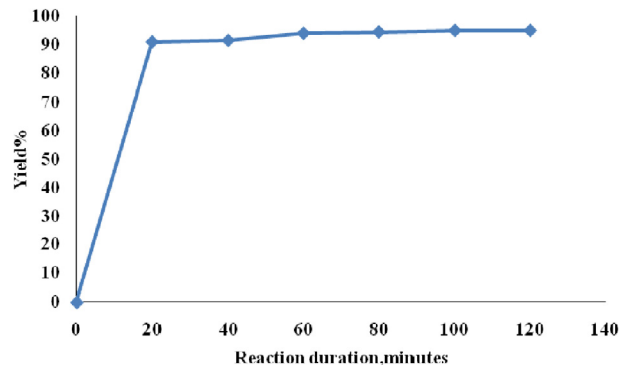


**Figure 4** Influence of the reaction temperature on the biodiesel yield.

**3.2.2.4. Influence of reaction duration.** The reaction period is an important factor that should be investigated from an economical point of view for it raises the production cost. Therefore, the influence of reaction period on the BD yield was investigated by using various reaction durations (20, 40, 60, 80, 100 and 120 min), while other conditions were kept constant (0.90% KOH, 6:1 methanol to oil molar ratio, 60°C reaction temperature and a stirring rate of 600 rpm). It was found that the BD yield increases with the increment of reaction duration as can be seen in Fig. 5. The highest yield of BD (95%) was obtained at 100 min reaction time. After this duration, no significant increase in the yield was observed.

### 3.3. Fuel properties of SMSO biodiesel

The properties of the BD produced from SMSO were determined in accordance with the ASTM standards and listed in Table 3. Each value was measured in triplicate, and the mean was recorded. The density of the BD produced from SMSO was (0.8810 g/mL). George et al. (2008) reported densities of biodiesels produced from sunflower, rapeseed and olive oils to be (0.8827, 0.8821 and 0.8815 g/mL), respectively. One of the most important properties of BD is viscosity. The higher viscosity of BD leads to poorer atomization and causes engine deposits. Therefore, viscosity of BD must be low (Rashed and Anwar, 2008a,b; Demirbas, 2008). The viscosity of the BD produced from SMSO was (4.50 mm<sup>2</sup> s<sup>-1</sup>), which is less than that reported for biodiesels produced from rubber seed and jatropha oils (5.81 and 5.65 mm<sup>2</sup> s<sup>-1</sup>), respectively (Ramadhas et al., 2005; Chhetri et al., 2008). However, the viscosity of SMSO biodiesel was within the required limits specified by the ASTM standards. A temperature at which a fuel produces a vapor that will ignite when exposed to a spark is called flash point (Rashed and Anwar, 2008a,b). The flash point of SMSO was 230. After acid treatment, it is reduced to 120. However, a great reduction in the flash point was after the alkaline transesterification, it reduced to 85. The suggested BD has a lower flash point compared to that produced from the rubber seed and jatropha (130 and 170), respectively (Ramadhas et al., 2005; Chhetri et al., 2008). The temperature at which the BD becomes non pourable on cooling is called the pour point. The pour point of the produced BD was -12. Such a value could be a good indicator that the BD is suitable for use in cold weather such as that prevailing in the north of Iraq in winter. The pour points reported for methyl esters produced from rubber seed oil was

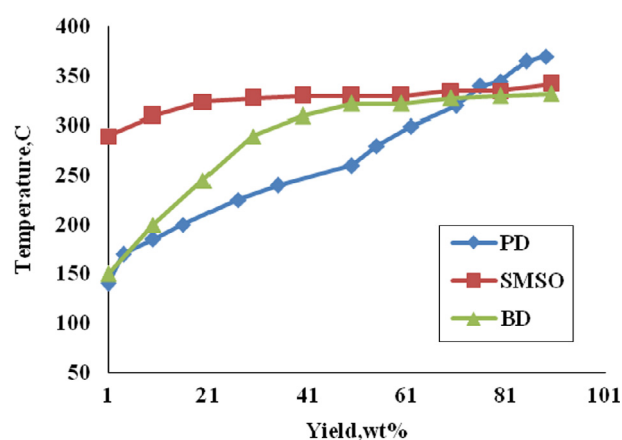


**Figure 5** Influence of the reaction duration on the biodiesel yield.

**Table 3** Properties of the methyl esters produced from SMSO.

Property	Method	SMSO	SMSO
		After acid esterification	Biodiesel
Density @ 16	ASTM D4052-91	0.9114	0.8780 ± 0.025
Kinematic viscosity @ 40 °C	ASTM D445	35.50	4.50 ± 0.20
Flash point °C	ASTM D93	120	85 ± 2
Combustion point °C	–	132	94 ± 2
Acid value mg KOH/g oil	ASTM D664	2.10	0.08 ± 0.01
Saponification value mg KOH/g oil	ASTM D5555-95	218	248 ± 1.0
Iodine number mg I <sub>2</sub> /100 oil	Hanus method	98	99 ± 1.0
Cloud point °C	ASTM D 2500	–2	–2 ± 0.5
Pour point °C	ASTM D 2500	–11	–12 ± 0.50
Conradson carbon Residue	ASTM D4530	0.10	0.03 ± 0.01
Refractive index @ 20 °C	D1747-09	1.467	1.445 ± 0.01
Cetane number	Willard (1997)	–	43.01
Higher heating value MJ/kg	Demirbas (2008)	39.13	41.53

(–8) (Ramadhas et al., 2005). The refractive index of BD was 1.455. This value is much lower than that of the parent oil. The degree of unsaturation can be expressed in terms of the iodine number. The iodine number of SMSO biodiesel was (99 mg I<sub>2</sub>/100 g oil). This value is lower than that specified by the ASTM standard (< 120 mg I<sub>2</sub>/100 g oil). The quality of BD can be expressed in terms of the acid value. It is the number of milligrams of KOH required to neutralize the acids exist in the sample (Zlatica, 2008). The acid value of SMSO was 13.60 mg KOH/g. This value reduced to below 2.0 mg KOH/g after acid esterification. After alkaline transesterification, the produced BD has an acid value of (0.08 mg KOH/g), which is much lower than the required limits (0.60 max) specified by the ASTM standard. Furthermore, the acid value of the suggested BD sample is much lower than that reported for the biodiesels produced from sunflower oil (0.24 mg KOH/g oil) (Rashid et al., 2008a,b), rice bran oil (0.44 mg KOH/g oil) (Nithya and Korla, 2011) and *Nicotiana tabacum* L. seed oil (0.66 mg KOH/g oil) (Veljkovic et al., 2006). The saponification value represents the number of milligrams of potassium hydroxide required to saponify 1 g of the sample. The saponification value of SMSO was 195 mg KOH/g. After the acid esterification, the value was reduced to 218 mg KOH/g. It was found that the BD produced from SMSO has a saponification value of 248 mg KOH/g. It is well known that the higher the saponification value is, the lower the molecular weight. The carbon residue of the BD produced from SMSO is 0.03%. The distillation curves of petro diesel, SMSO and BD are illustrated in Fig. 6 which indicates that the produced BD has lower initial boiling point (150) than its parent oil (290). This means that the BD is more volatile, and hence could be used as extra evidence for the TE process. In comparison with petro diesel (PD), it is clear that the initial boiling point of BD was close to that of PD. An important measure of the ignition quality of the diesel fuel is the cetane number. The greater the cetane number is, the more ignitable the fuel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number (Demirbas, 2009). The cetane number of the produced BD is 43.01. This value is lower than that reported for the BD produced from safflower and guindilla oils (52.32 and 59), respectively (Rashed and Anwar, 2008a,b; Martin et al., 2010). However, the lower value of the cetane number belongs to the high unsaturated fatty acid content in SMSO.

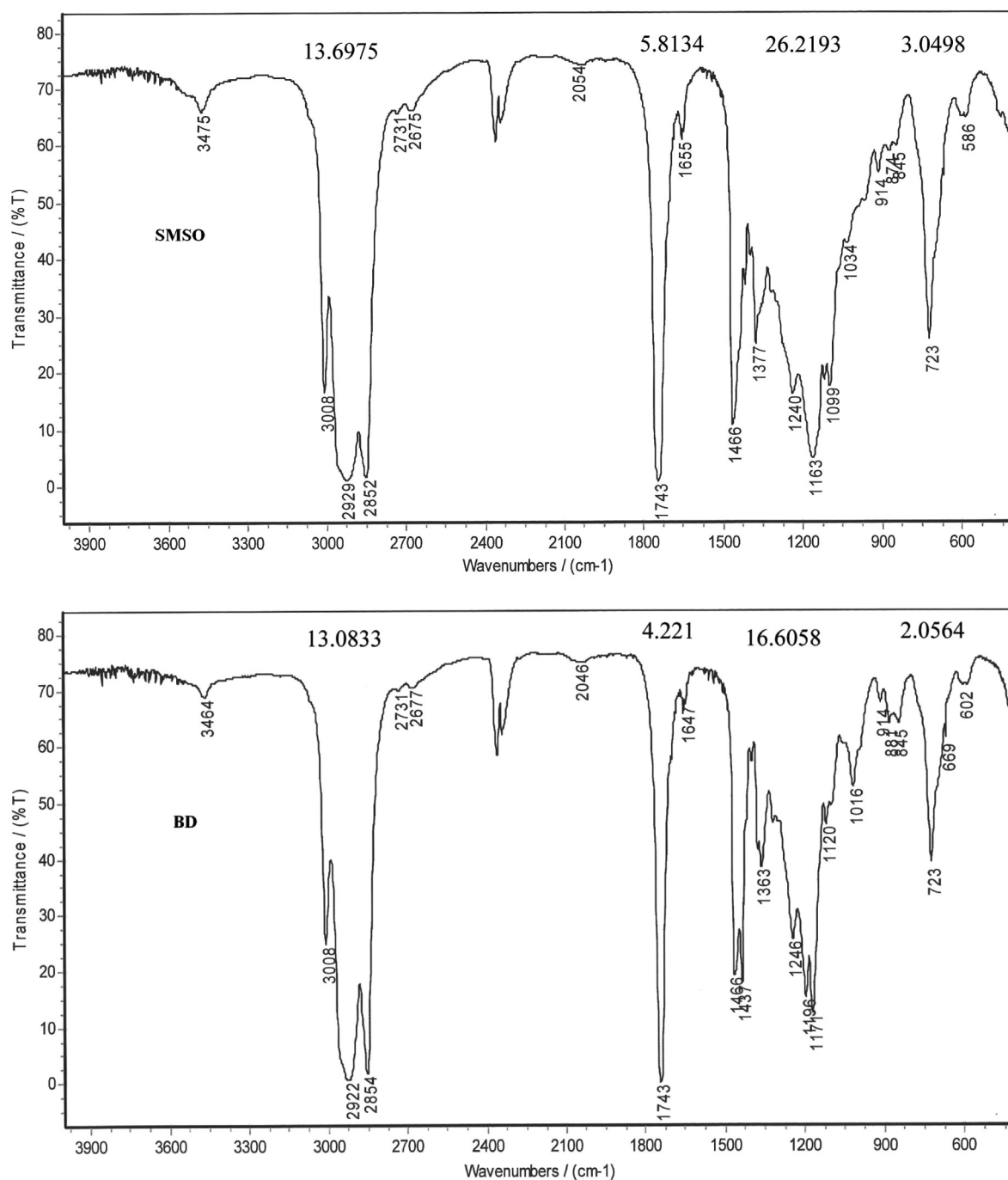
**Figure 6** Distillation curves of SMSO, BD and PD.

### 3.3.1. The FTIR measurements

The FTIR spectra of SMSO and the optimal BD fuel were measured for two purposes; the first is for the qualitative determination of some of the obtained characteristic bands, the second is for the quantitative determination by monitoring the TE reactions. The observed bands were as follows:

The absorption band at 3008–2854 cm<sup>-1</sup> refers to asymmetric and symmetric CH<sub>3</sub> stretching vibrations (–CO–O–CH<sub>3</sub>), 1466–1437 cm<sup>-1</sup> indicates the –C–H (alkane), 1246–1016 cm<sup>-1</sup> belongs to stretching vibration of the (–C–O) ester groups, and the absorption band at 1647 indicates (C=C) the stretching modes characteristic of olefins. The characteristic absorption band at 1743 cm<sup>-1</sup> refers to the ester carbonyl group (C=O). The FTIR spectra of SMSO and the BD fuel are shown in Fig. 7. The main differences observed between the infrared spectra of SMSO and the produced BD fuel are a small displacement of the stretching C=O band and stretching C–H band as well as the C–H bonding band of the BD to the lower energy. This is attributed to the substitution of the glycerol by the methoxy radical.

As already stated, the FTIR spectra were also used for quantitative determination to monitor the TE reaction. For this purpose, the area under the absorption peaks was calculated to give a strong support for the proceeding TE reaction. The area under the peaks of the parent oil and its optimal BD



**Figure 7** FTIR spectra of SMSO and the produced BD.

sample are depicted in Fig. 7 which shows the presence of distinct differences between the IR spectra of the oil and its BD, so that the area under the peak of each of the above bands in the original oil is affected due to the TE operation. The results indicate that the TE process is a successful means to alter the fuel properties of oil and transfer it into a more valuable fuel. The variations in the area values among the used oils are the best to point to the loss of glycerol from oil (glycerides) (Fadhil, 2010).

### 3.3.2. Thin layer chromatography

Thin layer chromatography is a rapid and simple technique used by several investigators to monitor the transesterification process (Santos et al., 2009; Haas et al., 2004; Danian and Milford, 1996; Hawash et al., 2009). In this study the transesterification of SMSO was monitored by the TLC technique by using silica gel plates as can be seen in Fig. 8 which shows that SMSO exhibits four spots, while only one spot appears in the BD. The latter could be an indication for the formation of the corresponding ester.



**Figure 8** TLC plates of SMSO and BD.

#### 4. Conclusions

Biodiesel fuel was developed from a novel feedstock viz. *S. marianum* L seed (SMSO). The results of this study indicate that SMSO can be used as a possible feedstock for the production of biodiesel. This was concluded from the high yield of biodiesel (95%) obtained under optimized reaction conditions. A two-step catalyzed transesterification viz. acid–base catalyzed transesterification was necessary to produce biodiesel from SMSO, because the latter has a higher free fatty acid content (6.80%). To reduce the FFA content in SMSO, esterification of SMSO was carried out by using various concentrations of HCl% w/w of oil with a 6:1 methanol to oil molar ratio at 60°C for 1 h. It was found that 1% HCl was optimal for esterification because it resulted in the minimum acid value (1.89 mg KOH/g oil). The oil that resulted from the esterification is converted into biodiesel through alkaline-catalyzed transesterification. The optimum conditions of this stage are 0.90% KOH w/w of oil, 6:1 methanol to oil ratio, 60°C reaction temperature and a duration of 100 min. A conversion of (95%) is obtained by using these optimum conditions of reaction. The fuel properties of the produced biodiesel were determined in accordance with the ASTM standard and found to conform with ASTM D 6751 specifications.

#### Acknowledgement

The authors are thankful to the University of Mosul, College of Science, Dept. of Chemistry for presenting facilities that made this work successful.

#### References

Alamu, O.J., Waheed, M.A., Jekayinf, S.O., 2008. Fuel 87 (8–9), 1529–1533.

- Alptekin, E., Canakci, M., 2010. Fuel 89, 4036–4037.
- Batidzirai, B., Faaij, A.P.C., Smeets, E., 2006. Energy Sustainable Dev. (1), 54–81.
- Bhatti, H.N., Hanif, M.A., Qasim, M., Rehman, A., 2008. Fuel 87, 2961–2967.
- Cankci, M., Sanli, H., 2008. J. Ind. Microbiol. Biotechnol. 35, 431–441.
- Chhetri, A.B., Tango, M.S., Budge, S.M., Watts, K.C., Rafiqul Islam, M., 2008. Int. J. Mol. Sci. 9, 169–180.
- Chung, K.H., Kim, J., Lee, K.Y., 2009. Biomass Bioenergy 33, 155–158.
- Danian, Z., Milford, A.H., 1996. Bioresour. Biotechnol. 57, 137–142.
- Demirbas, A., 2008. Fuel 87, 1744–1745.
- Demirbas, A., 2009. Biomass Bioenergy 33, 13–118.
- Dorado, M.P., Cruza, F., Palomara, J.M., López, F.J., 2006. Renew. Energy 31, 1231–1237.
- El-Mallah, M.H., El-Shami, S.M., Hassanein, M.M., 2003. Grasas Aceites 5494, 397–402.
- El-Mashad, H.M., Zhang, R., Roberto, J.A., 2008. Biomass Eng. 99, 220–227.
- Fadhil, A.B., 2010. Ph.D. Thesis, Mosul University, Iraq.
- Fadhil, A.B., Dheyab, M.M., Abdul-Qader, A.Y., 2012. JAAUBAS 11, 45–49.
- George, A., Ypatia, Z., Stamoulis, S., Stamatis, K., 2009. Energies 2, 362–376.
- Ghadge, S.V., Raheman, H., 2006. Bioresour. Technol. 97 (3), 379–384.
- Haas, M.J., Michael, J., Scott, K.M., Marmer, W.N., Foglia, T.A., 2004. JAOCS 81 (1), 83–89.
- Hawash, S., Kamal, N., Zaher, F., Kenawi, O., El Diwani, G., 2009. Fuel 88, 579–582.
- Knothe, G., Steidley, K.R., 2005. Fuel 84, 1059–1065.
- Koria, L., Thangaraj, T., 2010. J. Ecobiotechnol. 2 (5), 42–46.
- Malaya, N., Meher, L.C., Naik, S.N., Das, L.M., 2005. Biomass Bioenergy 32 (4), 354–357.
- Martin, R.S., De la Cerda, T., Uribe, A., Basilio, P., Jordln, M., Prehn, D., Gebauer, M., 2010. Fuel 89, 3785–3790.
- Mathiyazhagan, M., Ganapathi, A., Jaganath, B., Renganayaki, N., Sasireka, N., 2011. Int. J. Chem. Environ. Eng. 2 (2), 119–122.
- Meher, L.C., Dharmagadda, Vidya S.S., Naik, S.N., 2006. Bioresour. Technol. 97 (12), 1392–1397.
- Moghaddam, N.A., Akhavan, N., Tahvildari, K., Taghvaie, S., 2010. World Acad. Sci. Eng. Technol. 71, 615–619.
- Nithya, G., Koria, L., 2011. J. Ecobiotechnol. 3 (12), 07–09.
- Ramadhass, A.S., Jayaraj, S., Muraleedharan, C., 2005. Fuel 84, 335–340.
- Rashed, U., Anwar, F., 2008a. Energy Fuels 22 (2), 1307–1310.
- Rashed, U., Anwar, F., 2008b. Fuel 87, 260–273.
- Rashid, U., Anwar, F., Moser, B.R., Knothe, G., 2008a. Bioresour. Technol. 99, 8175–8179.
- Rashid, U., Anwar, F., Moser, B.R., Ashraf, S., 2008b. Biomass Bioenergy 32, 1202–1205.
- Sahoo, P.K., Das, L.M., Babu, M.K.G., Naik, S.N., 2007. Fuel 86, 448–454.
- Santos, F.P.F., Rodrigues, S., Fernandes, F.A.N., 2009. Fuel Process. Technol. 90, 312–316.
- Veljkovic, V.B., Lakićević, S.H., Stamenkovic, O.S., Todorovic, Z.B., Lazić, M.L., 2006. Fuel 85, 2671–2675.
- Willard, W.P., 1997. Engineering Fundamentals of the Internal Combustion Engine. Prentice-Hall Limited, Singapore, pp. 323–325.
- Zhu, H., Wu, Z., Chen, Y., Zhang, P., Duan, S., Liu, X., Mao, Z., 2006. Chin. J. Catal. 27, 391–396.
- Zlatica, J.P., 2008. Fuel 87, 3522–3528.