

Production of Biodiesel through Base-Catalyzed Transesterification of Safflower Oil Using an Optimized Protocol

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Production of biodiesel through optimized base-catalyzed transesterification of safflower oil was investigated. Various experimental variables, such as the oil/methanol molar ratio (1:3, 1:6, 1:9, 1:12, 1:15, and 1:18), temperature (30, 45, and 60 °C), rate of stirring (180, 360, and 600 rpm), catalyst concentration (0.25, 0.50, 0.75, 1.00, 1.25, and 1.50%), and catalyst types (KOH, NaOH, KOCH₃, and NaOCH₃) were adopted. An oil/methanol molar ratio of 1:6, sodium methoxide catalyst concentration of 1.00%, mixing intensity of 600 rpm, and reaction temperature of 60 °C offered the best safflower oil fatty acid methyl esters (biodiesel) yield (98%). Characterization of the fatty acid methyl esters (FAMES) was accomplished by gas–liquid chromatography (GLC). Fuel properties, such as density, specific gravity, kinematic viscosity, high heating value, cetane number, flash, cloud, pour, and cold filter plugging points, copper strip corrosion, acid value, and sulfur, water, and ash contents of the biodiesel produced were compatible with American Society for Testing and Materials (ASTM) D 6751 and EN 14214 specifications, where applicable. However, the cold filter plugging, cloud, and pour points were somewhat higher than the conventional diesel fuel. Results of the present investigation demonstrated that the biodiesel produced through methanolysis of safflower oil under a given set of experimental conditions has fuel properties quite comparable to those of mineral diesel and thus may be explored for potential applications in compression–ignition engines.

1. Introduction

Currently, the energy requirements of the world are mainly met through fossil fuels, such as gasoline, petroleum-based diesel, and natural gas. Such fossil-derived resources are scarce toward fulfilling the future energy demands and meeting the challenges of rapid human population growth and technological developments. The anticipated decreasing supply of fossil fuels coupled with environmental safety concerns has provoked the efforts to encourage the use of bio-based fuels as renewable energy sources. Several types of biofuels, such as vegetable oil/animal fat (raw, processed, or used), methyl esters from oil/fat, and ethanol or liquid fuels from biomass have been searched as a replacement for gasoline and petroleum diesel.¹

The uses of biodiesel as a renewable, biodegradable, nontoxic, and eco-friendly neat fuel or in blends with petroleum-based fuels are fascinating.^{2,3} The European Union (EU) and other developed countries, including United States and Malaysia, are encouraging the use of biodiesel. The EU biodiesel production capacity of about 6.1 million metric tons (MMT) in 2006 was expected to reach the figure of 8.0 MMT by the year 2007.^{1,4}

“Biodiesel” is defined as the monoalkyl esters of long-chain fatty acids derived from vegetable oils/animal fats. Several types

of conventional and nonconventional vegetable oils and animal fats have been employed for the production of biodiesel, including used oils from the frying industry: soybean oil, rapeseed oil, tallow, rubber seed oil, and palm oil.^{1,5–7} The production of biodiesel comprises the conversion of vegetable oils/animal fats using methanol and a catalyst to produce fatty acid methyl esters (FAMES) and crude glycerin through a process termed “transesterification”. The transesterification is an equilibrium reaction and occurs essentially by mixing the reactants. In the transesterification of the vegetable oils, triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acid alkyl esters and glycerol. The stoichiometric reaction needs 1 mol of a triglyceride and 3 mol of an alcohol. However, an excess of alcohol is favored to increase the yield of alkyl esters and to allow their better separation from the glycerol layer. The alkali-catalyzed transesterification of vegetable oils, often used for commercial purposes, is known to proceed much faster than the acid-catalyzed transesterification. However, the experimental variables, such as substrate oil, methanol/oil molar ratio, reaction temperature and time, catalyst concentration and type, and mixing intensity can affect the yield and quality of end-use products (methyl esters/biodiesel and glycerol).^{8,9}

Safflower (*Carthamus tinctorius* L.), a member of the Compositae or Asteraceae family has long been cultivated mainly for its seed (source of an edible oil), colorful petals

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(valued as a food coloring and flavoring agent), and also as a source of red and yellow dyes for clothing and food in the Far East, Central and North Asia, America, North Africa, Europa, and Caucasia.^{10,11} India, U.S.A., and Mexico are the principle producers of safflower; however, the crop has also been cultivated in many other countries, such as Kazakhstan, Ethiopia, Argentina, China, Uzbekistan, Australia, Russian Federation, Pakistan, and Spain.^{10,11} Safflower seeds are a potential source of linoleic acid (C18:2 *n*-6) rich oil with an approximate yield of 36–41%. Another type, i.e., high oleic safflower oil, has also been introduced in the marketplace.

Safflower, although recognized as one of humanity's oldest crops, is still categorized as a minor crop. The world's safflower seed production is around 600 000 tons per year.¹¹ In Pakistan, cottonseed is the major oil seed crop, accounting for 67% share of the domestic production of edible oils, followed by canola oil at 19.6%. The remaining, 13.4% mainly comes from sunflower oil. Although safflower has been grown for decades in Pakistan as a source of dye, folk medicine, and human food, it did not attract any significant attention as an oil seed crop and its cultivation had been limited until recently.¹²

Domestic renewable energy resources can play an important role in fulfilling the energy demands of a country, thus contributing and reducing its dependence on fossil-derived fuels. Pakistan, similar to other developing countries in south Asia and elsewhere in the world, is also facing serious challenges in meeting the country's energy demands. The existing petroleum-based energy resources of Pakistan are insufficient to meet the domestic needs, resulting in an expenditure of huge amounts of foreign exchange (ca. 5.97 billion U.S.\$ for the year 2005–2006) for the import of petroleum and petroleum products. In view of rapidly growing energy demands, exploration of some aboriginal, renewable energy resources has to play a crucial role. The present study was an attempt to evaluate the potential of indigenously available safflower oil for the production of biodiesel, using a base-catalyzed reaction. The reaction variables, such as the oil/methanol molar ratio, temperature, rate of stirring, catalyst concentration, and catalyst types were optimized for better yield and high quality of the biodiesel produced. The important physicochemical properties of the resultant biodiesel from safflower oil [safflower oil methyl esters (SOME)] were also determined to compare with rapeseed oil methyl esters (RME) and number 2 diesel fuel (D2).

2. Experimental Section

2.1. Materials. The seeds of safflower (*C. tinctorius*) were procured from Ayub Agricultural Research Institute (AARI), Faisalabad, Pakistan. Pure standards of FAMES were obtained from Sigma Chemicals Co. (St. Louis, MO). Methanol, *n*-hexane, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide, and anhydrous sodium sulfate were from Merck (Darmstadt, Germany). All of the chemicals used were analytical-reagent-grade, unless stated otherwise.

2.2. Extraction of Oil. The seeds (300 g) in each batch of safflower were crushed and then fed to a Soxhlet extractor fitted with a 2 L round-bottomed flask and a condenser. The extraction was executed on a water bath for 6 h with 1.0 L of *n*-hexane. The solvent was distilled off under vacuum in a rotary evaporator (Eyela,

N-N Series, Rikakikai Co. Ltd., Tokyo, Japan) at 45 °C, and the oil was recovered.

2.3. Preliminary Evaluation of Safflower Oil. The extracted safflower oil was analyzed for some important chemical properties. The acid value, iodine value, peroxide value, and saponification number of the oil were determined following the standard American Oil Chemists' Society (AOCS) methods F 9a-44, Cd 1-25, Cd 8-53, and Cd 3-25, respectively.¹³

2.4. Transesterification of Safflower Oil. Experiments were designed to ascertain the effect of catalyst type and concentration, reaction temperature, oil/methanol ratio, and stirring intensity on the transesterification of safflower oil. The catalysts types were varied as sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide. The catalyst (NaOCH₃) concentrations were used as 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50%. The reaction temperatures were opted as 30, 45, and 60 °C. The oil/methanol molar ratio were set as 1:3, 1:6, 1:9, 1:12, 1:15, and 1:18. The stirring intensity was varied as 180, 360, and 600 rpm.

The transesterification was carried out using a 1 L round-bottomed reactor, equipped with a thermostat, mechanical stirrer, sampling outlet, and condensation systems. This installation was consistent with that described in the literature.^{14,15} Briefly, the safflower seed oil (500 g) was preheated to the set temperatures (30, 45, and 60 °C) on a heating plate before starting the reaction. A fixed amount of freshly prepared alcoholic solutions of catalysts were added into the oil established for each experiment and mixed, taking this moment as time zero of the reaction. At consistently spaced periods, 2 cm³ of the sample was withdrawn for chromatographic analysis. Each experiment was allowed to prolong for 120 min conduct to ensure the complete conversion of the fatty acids into FAMES.

2.5. Separation and Purification of FAMES/Biodiesel. After the completion of the reaction, the reaction mixture was allowed to cool and equilibrate, resulting in the separation of two phases. The upper phase consisted of SOME, and the lower phase contained the glycerol, the excess methanol, the remaining catalyst together with the soaps formed during the reaction, and some entrained methyl esters and partial glycerides. After separation of the two layers, the upper SOME layer was purified by distilling the residual methanol at 80 °C. The remaining catalyst was removed by successive rinses with distilled water. Finally, the residual water was eliminated by treatment with Na₂SO₄, followed by filtration. The lower phase was acidified with a calculated amount of sulfuric acid, to neutralize any unreacted potassium hydroxide and decompose the soaps formed during the transesterification. The resulting mixture was subjected to distillation at 80 °C under a moderate vacuum to recover the excess methanol. This facilitated the separation of glycerol from entrained methyl esters and soaps.

yield of methyl esters = (grams of methyl esters produced / grams of oil taken for the reaction) × 100

2.6. Characterization of SOME. The SOME/biodiesel were analyzed on a SHIMADZU gas chromatograph, model 17-A, equipped with a flame ionization detector (FID). Separation was performed on a methyl-lignocerate-coated polar capillary column SP-2330 (30 m × 0.32 mm, 0.20 μm; Supelco, Inc., Bellefonte, PA). Nitrogen was used as a carrier gas at a flow rate of 3.0 mL/min. The column temperature was programed from 180 to 220 °C at the rate of 5 °C/min. Initial and final temperatures were held for 2 and 10 min, respectively. The injector and detector were set at 230 and 250 °C, respectively. A sample volume of 1.0 μL was injected using a split mode, with the split ratio of 1:75. FAMES were identified by comparing their relative and absolute retention times to those of authentic standards. Heptadecanoic acid (C17:0)

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was used as an internal standard. The external calibration method was adopted for standardization. The quantification was performed by a chromatography station for Windows (CSW32) data-handling software (Data Apex Ltd., CZ-158 00 Pague 5, Czech Republic). The fatty acid composition was reported as a relative percentage of the total peak area.

2.7. Fuel Properties of SOME. The samples of biodiesel produced were tested for their fuel properties. The density was determined by a digital density analyzer (PAAR, DMA 38) using American Society for Testing and Materials (ASTM) D 5002. The specific gravity (15 °C) of the biodiesel was measured by ASTM D 287. The kinematic viscosities were determined at 40 °C, using a calibrated viscometer. The procedure of ASTM D 445 was followed. Analyses of the higher heating values were estimated by following ASTM D 4868. The cetane number was determined following ASTM D 613. The flash point was determined by a Pensky–Martens closed-cup tester (ISL, model FP93 5G2), using ASTM D 93. The cold filter plugging point was determined using a CFPP apparatus (ISL, model CPP97-2) following the procedure of ASTM D 6371. Cloud and pour point determinations were made using ASTM D 2500 and ASTM D 97. The sulfur content was determined by energy-dispersive X-ray fluorescence spectrometry (OXFORD, Model Lab-X3000) following ASTM D 4294. Detection of copper corrosion was made by the copper strip tarnish test following ASTM D 130. Ash content was determined according to ASTM D 874. The water content was estimated following ASTM D 95. The acid value of the biodiesel was measured following ASTM D 974. The ester and methanol contents were studied using EN 14103 and EN 14110, respectively. The free and bound glycerin was determined by ASTM D 6584. Each experiment was conducted in triplicate, and the data are reported as the mean \pm standard deviation (SD).

3. Results and Discussion

3.1. Preliminary Chemical Properties of Safflower Oil.

The safflower oil (average molecular weight = 885.47) as analyzed before the initiation of the transesterification reaction at the preliminary stage exhibited an iodine value of 141.52 g of I/100 g of oil, acid value of 0.35 mg of KOH/g of oil, and peroxide (mequiv/kg of oil) and saponification values (mg of KOH/g of oil) of 188.15.

3.2. Optimization of the Catalyst Type and Concentration. The effectiveness of catalyst types and concentration toward transesterification of safflower oil was evaluated to find the catalyst with the best catalytic activity. The most commonly used catalysts (potassium hydroxide, sodium hydroxide, potassium methoxide, and sodium methoxide) were tried in this study. The screening data for the tested catalysts are presented in Figure 1. Reaction products are presented as a percentage of methyl esters of fatty acids in the reaction mixture. Figure 1 shows that, among the tested catalysts, sodium methoxide exhibited the highest yield of methyl esters during the transesterification of safflower oil with methanol. Moreover, it can be observed that sodium and potassium methoxides offered the higher yields when compared to their corresponding hydroxides. In conflict to our findings, some earlier studies in the literature revealed that, during the transesterification of *Brassica carinata* and *Pongamia pinnata* oils with methanol, potassium hydroxide exhibited the best catalyst activity.^{16,17}

The concentration of the catalyst was an important parameter studied. The catalyst NaOCH₃ concentrations opted in this study were 0.25–1.50% (on the basis of the weight of raw oil). The operational conditions for the production of biodiesel from

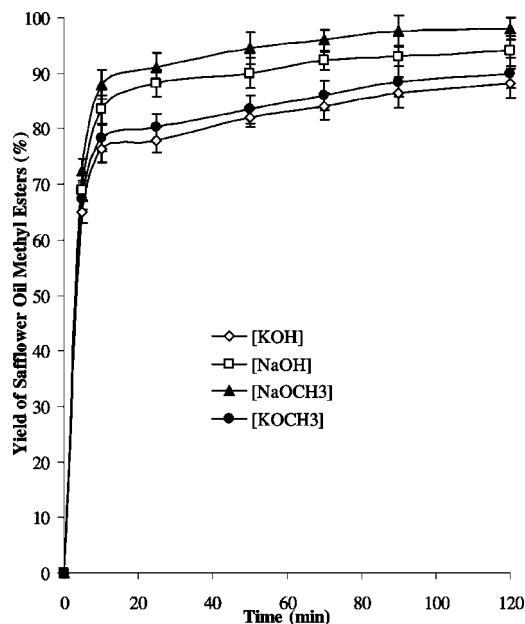


Figure 1. Effect of the catalyst type on the yield of SOME (1:6 oil/methanol molar ratio, 600 rpm rate of stirring, 60 °C reaction temperature, and equimolecular catalyst concentration).

safflower oil during the whole transesterification reaction were fixed at a reaction temperature of 60 °C, a reaction time of 120 min, an oil/methanol molar ratio at 1:6, and a rate of stirring at 600 rpm.

The results clearly indicated that the optimum concentration of NaOCH₃ required for effective transesterification of safflower oil was 1.00%. It was observed that if the NaOCH₃ concentration was decreased below or increased above the optimum, there was no significant ($p > 0.05$) increase in the biodiesel yield; nevertheless, there was an increased formation of glycerol and emulsion. This might be attributed to the free acid content of the oil. With the increase in the concentration of catalyst, there was a decrease in the yield of methyl esters. This was in accordance with the results of Dorado et al.¹⁷ and Encinar et al.,¹⁸ who reported that the formation of soap in the presence of a high amount of catalysts increases the viscosity of the reactants, thus resulting in a lower yield. The variation in the NaOCH₃ concentration versus the percentage of ester yield is shown in Figure 2. It could be observed from the data of Figure 2 that the maximum ester yield of 98% was achieved using a 1.00% NaOCH₃ concentration. Our results qualitatively differed compared to those of Dorado et al.¹⁷ and Encinar et al.,¹⁸ who reported that KOH offered the maximum ester yield for the methanolysis of *P. pinnata* oil and used frying oil, respectively.

3.3. Optimization of the Reaction Temperature. To optimize the influence of the reaction temperature on methyl esters formation, temperature variations adopted in this study were 30, 45, and 60 °C. The constant reaction time of 120 min, optimized catalyst type and NaOCH₃ concentration of 1.0% as obtained in the previous section, oil/methanol molar ratio of 1:6, and rate of stirring at 600 rpm respectively, which offered the best ester yield, were maintained with the temperature variations for the production of biodiesel from safflower oil.

As specified by Figure 3, the transesterification proceeded to more than 80% completion after 10 min, regardless of the temperature variations. After 120 min, the reaction was completed up to 98.0, 95.5, and 88.9% at 60, 45, and 30 °C,

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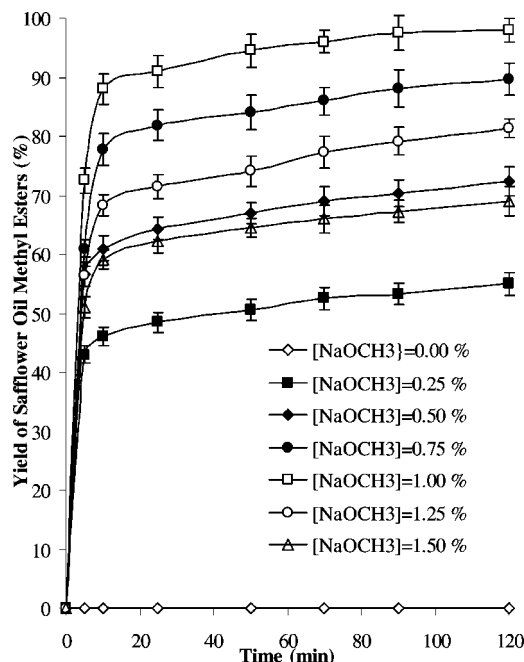


Figure 2. Effect of the NaOCH_3 concentration on the yield of SOME (1:6 oil/methanol molar ratio, 600 rpm rate of stirring, and 60 °C reaction temperature).

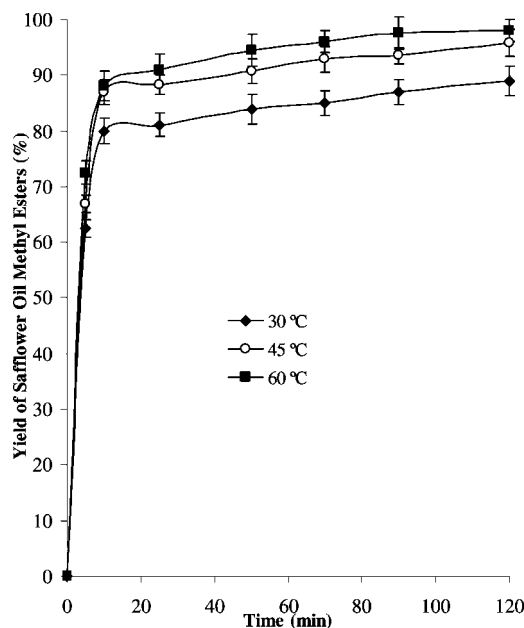


Figure 3. Effect of the temperature on the yield of SOME (1.0% NaOCH_3 , 1:6 oil/methanol molar ratio, and 600 rpm rate of stirring).

respectively. This result is in accordance with previous studies^{13,16} that correlated reaction temperature and time. As such, it is recommended that methanolysis of safflower oil can be performed at 60 °C. This is in agreement with the previous studies.^{18–20}

3.4. Optimization of the Oil/Methanol Molar Ratio. The methanolysis of safflower oil was carried out in six experiments, whereby the oil/methanol molar ratio (1:3, 1:6, 1:9, 1:12, 1:15, and 1:18) was varied to establish the effect of the methanol

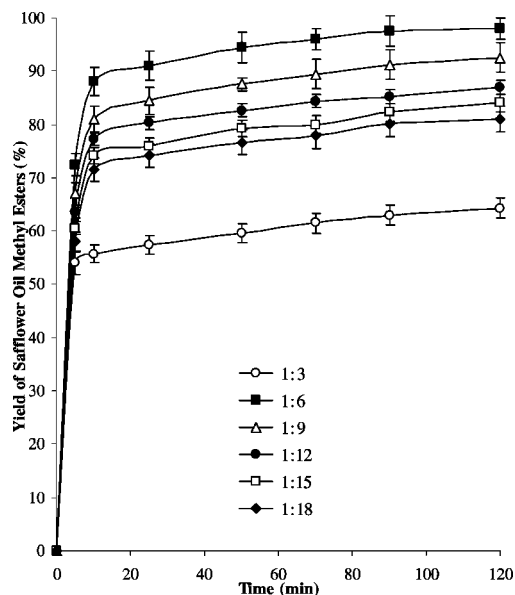


Figure 4. Effect of the oil/methanol molar ratio on the yield of SOME (1.0% NaOCH_3 , 600 rpm rate of stirring, and 60 °C reaction temperature).

concentration on SOME production. In all experiments, 600 rpm rate of stirring, 60 °C reaction temperature, and 1.00% NaOCH_3 were employed. The best possible yield (98%) of SOME was afforded with a molar ratio of 1:6 (Figure 4). The stoichiometric ratio of oil/methanol (1:3) offered the lowest conversion (61%). Higher quantities (beyond 1:6) of methanol exhibited a detrimental effect on SOME production, as is evident by steadily lower yields with the increase in the molar ratio from 1:6 to 1:18. At molar ratios of oil/methanol higher than 1:6, separation of esters from glycerol was problematic. The excess methanol hinders gravity decantation, so that the apparent yield of SOME may decrease because a portion of the glycerol remains in the biodiesel phase.²¹

Our results of optimum yield (98%) of SOME with an oil/methanol molar ratio of 1:6 are in agreement with earlier studies,^{3,9,16,21,22} which reported optimum conversion of various vegetable oils with a molar ratio of 1:6.

3.5. Optimization of the Rate of Stirring. The effect of stirring on SOME production was investigated in three experiments by differing stirring rates (180, 360, and 600 rpm). In all experiments, an oil/methanol molar ratio of 1:6, a reaction temperature of 60 °C, and a NaOCH_3 catalyst concentration of 1.00% were used. As depicted from Figure 5, a direct correlation was elucidated between the stirring rate and SOME yield; i.e., as the rate of agitation was increased, an increase in yield was observed. Accordingly, a mixing rate of 600 rpm afforded the optimum conversion of safflower oil to SOME (98%). This is in accordance with earlier studies,^{9,23,24} which concluded that elevated stirring rates promoted the homogenization of reactants, leading to higher methyl ester yields.

3.6. Quality of SOME. The gas–liquid chromatography (GLC) evaluation of the SOME, as shown in Figure 6, demonstrated a typical pattern of fatty acids. The main methyl ester was linoleic acid (75.98%), followed by oleic (14.20%),

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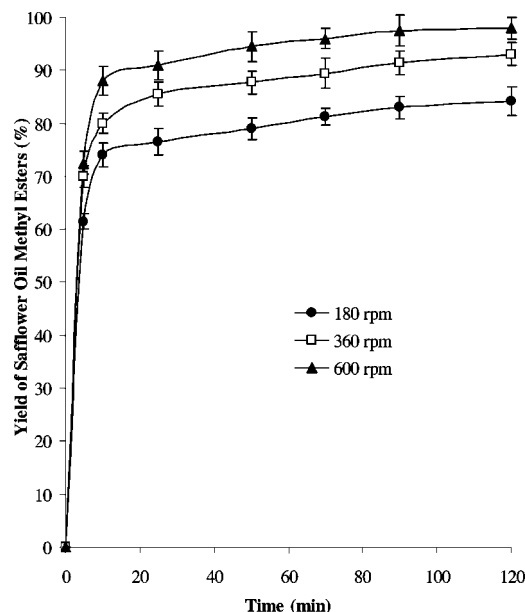


Figure 5. Effect of the rate of stirring on the yield of SOME (1.0% NaOCH_3 , 1:6 oil/methanol molar ratio, and 60 °C reaction temperature).

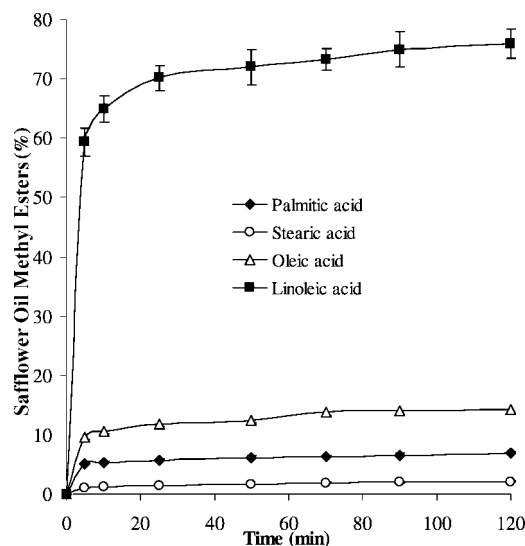


Figure 6. Evaluation of the SOME concentration with time (1.0% NaOCH_3 , 1:6 oil/methanol molar ratio, 60 °C reaction temperature, and 600 rpm rate of stirring).

palmitic (6.85%), and stearic (2.11%) acids. The optimal methyl esters concentration (97.62%) was achieved in almost 90 min of the reaction. The curve displayed an asymptotic tendency with respect to time and became stable after 90 min. These trends of results were in agreement with our previous study for the production of biodiesel from rapeseed oil.⁹ These tendencies observed in our present study were also similar to those of Encinar et al.¹⁸ for the production of biodiesel using *Cynara cardunculus* oil.

The present GLC results further supported the fact that SOME produced under an optimized set of experiments had their free and total glycerol contents within ASTM D 6751 specifications. Non-optimized methanolysis experiments yielded impure SOME with substantial quantities of free and bound glycerol. As expected, impurities had deleterious effects on the resultant fuel properties (results not shown), especially with regard to diminished temperature performance, manifested by increased cloud, pour, and cold filter plugging points (CP, PP, and CFPP,

respectively), and increased kinematic viscosity (40 °C) in comparison to pure SOME.

3.7. Fuel Properties of SOME/Biodiesel. The important fuel properties [density (15 °C), specific gravity (15 °C), kinematic viscosity (40 °C), CP, PP, CFPP, flash point, combustion point, cetane number (CN), high heating value (HHV), copper strip corrosion (3 h at 50 °C), acid value, sulfur, water, and ash contents] of SOME as measured according to accepted ASTM methods are depicted in Table 1. These properties of SOME investigated in this study satisfied nearly all prescribed ASTM D 6751 and EN 14214 specifications, where applicable.

3.7.1. Density and Specific Gravity. Density is an important property of biodiesel. The density of biodiesel produced from safflower oil was 874 kg/m³. Rashid and Anwar⁹ and Alcantara et al.²⁵ reported the densities of biodiesel produced from rapeseed and soybean oils to be 880 and 890 kg/m³, respectively. The density of the conventional diesel ranges between 825 and 835 kg/m³. The specific gravity, which is the ratio of the density of the liquid/density of water, of the biodiesel produced from safflower oil in the present study, was 0.887 (Table 1). The specific gravity of mineral diesel is ca. 0.85. Fuel injection equipment operates on a volume metering system; hence, a higher density or specific gravity for biodiesel may result in the delivery of a slightly greater mass of fuel.

3.7.2. Kinematic Viscosity. The kinematic viscosity of a biodiesel, which is significantly influenced by the feedstock used, of the SOME in the present work as a function of the temperature at 40 °C was 4.29 mm²/s (Table 1). The higher viscosity of biodiesel may cause operational problems, such as engine deposits. Thus, the biodiesel viscosity must be low.²⁶ Usta,²¹ Demirbas,²⁷ Rashid and Anwar,⁹ and Holser and Harry-O'Kuru²⁸ reported the viscosities of biodiesels produced from tobacco, crambe, rapeseed, soybean, and milkweed seed oils to be 3.5, 5.12, 4.15, 4.6, and 4.1 mm²/s, respectively. The ASTM standard D 6751 prescribed an acceptable viscosity at 40 °C range for biodiesel of 1.9–6.0 mm²/s. The kinematic viscosity (40 °C) offered by SOME in the present work satisfied the limits of ASTM standard D 6751 and EN 14214 (3.5–5.0 mm²/s) specifications as well.

3.7.3. Higher Heating Value (HHV). HHV is a measure of the energy produced when the fuel is burnt completely, which also determines the suitability of biodiesel as an alternative to diesel fuels. Table 1 showed the HHV value of SOME produced to be 45.2 MJ kg⁻¹. In the standard ASTM D 6751, specifications about HHV of the biodiesel do not exist but considering that the HHV of the diesel fuel was about 45 MJ kg⁻¹. Moreover, Usta²¹ investigated the heating value for biodiesel produced for tobacco seed oil to be 39.8 MJ kg⁻¹.

3.7.4. Cetane Number. The cetane number, which measures the tendency of the fuel to self-ignite at the temperature and pressure in the cylinder when the fuel is injected, is defined by ASTM D 613.²⁹ A higher cetane number indicates that the fuel is more ignitable. As shown in Table 1, the cetane number of the biodiesel produced from the safflower oil was 52.3. Georgogianni et al.³⁰ and Usta²¹ reported that the cetane numbers

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Table 1. Characteristics of SOME and Comparison to RME and D2

fuel property	ASTM method used	SOME ^a	RME ^{b,d}	D2 ^c
density (15 °C, kg/m ³)	D 5002	874 ± 9.61	880	847
specific gravity (15 °C)	D 287	0.88 ± 0.02	0.869	0.85
kinematic viscosity (40 °C, mm ² /s)	D 445	4.29 ± 0.12	4.15	2.39
high heating value (MJ/kg)	D 4868	45.21 ± 1.58	44.9	45.2
cetane number	D 613	52.32 ± 1.15	51	46
flash point (°C)	D 93	176.00 ± 3.28	165	85
cold filter plugging point (°C)	D 6371	−6.00 ± 0.12	−9	
cloud point (°C)	D 2500	−2.00 ± 0.05	−3	−19
pour point (°C)	D 97	−8.00 ± 0.25	−9	−23
copper strip corrosion (50 °C, 3 h)	D 130	1a	1a	3
acid value (mg of KOH/g)	D 664	0.28 ± 0.02	0.37	
sulfur (%)	D 4294	0.0112 ± 0.0003	0.0095	
water (%)	D 95	<0.01	<0.01	
ash (%)	D 874	0.031 ± 0.002	0.022	
ester content (%)	EN 14103	97.67 ± 3.41		
methanol content (%)	EN 14110	0.170 ± 0.002		
free glycerin (%)	D 6584	0.016 ± 0.001		
total glycerin (%)	D 6584	0.225 ± 0.005		

^a SOME = safflower oil methyl esters. ^b RME = rapeseed methyl esters. ^c D2 = number 2 diesel fuel. ^d From ref 9.

of biodiesel produced from used soybean and tobacco seed oil were found to be 53.7 and 51, respectively.

3.7.5. Flash Point. The flash point of a biodiesel is determined by ASTM D 93.²⁹ It is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame. The biodiesel produced from safflower oil had a flash point (176 °C) greater than conventional diesel (Table 1). A higher value of the flash point is often correlated with a reduced risk of fire. This feature provides an advantage of biodiesel over mineral diesel.

3.7.6. Cloud, Pour, and Cold Filter Plugging Points. One of the major problems associated with the use of biodiesel is poor flow properties at low temperature as indicated by relatively high cloud points (CP), pour points (PP), and cold filter plugging points (CFPP) (Table 1). The values of CP and PP for the biodiesel produced in the present work were found to be −2 and −8 °C, respectively (Table 1). CFPP tests were conducted according to ASTM D 6371. This value was −6 °C. These points must be sufficiently low; for example, if the biodiesel is frozen, the motor will not start. According to ASTM standard D 6751, no limit is given, rather a “report” is specified for CP, PP, and CFPP. The reason is that the climate conditions in the world vary considerably, thus affecting the needs of biodiesel users in a specific region.

3.7.7. Sulfur, Water, and Ash Contents. The amount of total sulfur in SOME was determined by ASTM D 4294, using wavelength-dispersive X-ray fluorescence spectrometry (OXFORD, model Lab-X3000). As shown in Table 1, it is obvious that, in contrast to conventional diesel fuels (sulfur content of 50 ppm), the biodiesel produced from safflower oil/SOME in the present work exhibited a very low level of sulfur (0.0112%). The sulfur content in SOME was detected to be less than 1 ppm, one of the major advantages of biodiesel. In biodiesel obtained from used soybean oil, the sulfur content was 0.03 ppm.³⁰ Low sulfur content of biodiesel helps to protect both the environment and engine life. The water content of the SOME was measured using a standard test specified by ASTM D 95.²⁹ In the present work, the investigated water content for SOME was <0.01%. Water always produces negative effects because the presence of water in diesel causes soap formation and reduces catalyst effectiveness resulting in low efficiency.³¹ The water contents of the SOME in our work was within the standard specified by ASTM D 95²⁹ (0.050% maximum). Ash content

depicts the amount of inorganic contaminants, such as abrasive solids and catalyst residues, and the concentration of soluble metal soaps contained in a fuel sample. ASTM D 874²⁹ is the standard test method for determining sulfated ash from lubricating oils and additives. It could be seen from Table 1 that SOME had the sulfated ash of 0.031% by weight.

3.7.8. Acid and Copper Strip Corrosion Values. The acid value is a simplistic method for monitoring fuel quality. The acid value was estimated using ASTM D 664.²⁹ The acid value of the biodiesel produced in the present work was 0.28 mg of KOH/g (Table 1). ASTM D 664²⁹ specifies a limit of 0.5 (maximum) mg of KOH/g of an acid value for a biodiesel. ASTM D130 was adopted to measure the level of copper corrosion that would occur if biodiesel was used in any application where metals, such as copper, are present.³² The values of the copper strip corrosion test for the investigated SOME ranged within the limits specified by the standard ASTM D 6751 (number 3 maximum).

4. Conclusion

The transesterification of safflower oil yielded biodiesel with properties similar to those of mineral diesel. The oil/methanol molar ratio was one of the variables that had the most prevalent influence on the transesterification process. Within the range of molar ratios employed, the best results were obtained for 1:6. The catalyst, sodium methoxide, offered the highest ester yield (98%) at an optimum concentration of 1.00%. The influence of the temperature was also important. The best results were obtained at 60 °C. The rate of stirring was also the variable that had an effect on the process. The best yield was obtained at 600 rpm. Important fuel properties of SOME were compared well to ASTM D 6751 and EN 14214 specifications, where applicable. Therefore, we conclude that SOME is an acceptable substitute for D2 and other oil seed crop methyl esters for combustion in compression-ignition (diesel) engines in regions that use ASTM D 6751 specifications for fuel quality.

5. Safflower Biodiesel Economy

Efforts were also made to evaluate the economic feasibility of safflower biodiesel. Economical feasibility of biodiesel varies depending upon the feedstock, geographical area,

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(32) Gerpen, J. V.; Shanks, B.; Prusko, R.; Clements, D.; Knothe, G. National Renewable Energy Laboratory, 2004, NREL/SR-510-36244.

variability in crop production from season to season, and other attributes, such as market factors and environmental benefits. The rough projection for the cost of laboratory-scale biodiesel production from safflower oil is about 1.0 U.S.\$/L. The estimated price of safflower oil biodiesel may appear a bit high, but this price should be considered against the absence of any kind of subsidies to farmers. The profits from selling byproducts, i.e., glycerin for industrial uses and seed cake as animal feed can bring additional income for the producers and thus may reduce the selling price of biodiesel to an estimated 0.75 U.S.\$/L. In comparison to the current pretax petroleum-based diesel priced at 0.65 U.S.\$/L in

Pakistan, the biodiesel from safflower oil is not so economically feasible under existing circumstances. However, more research and advancements in biodiesel technology coupled with large-scale cultivation of safflower crop in Pakistan and additional subsidies from the government for producers may lead to further reduction of the cost of this renewable fuel. Further on, there is a real need to appraise the environmental benefits of producing biodiesel and to consider such attributes while determining the cost incurred in the production of such green fuels.

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