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Methyl Ester from Safflower Seed Oil of Turkish Origin as a Biofuel for Diesel Engines

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ABSTRACT

The primary problems associated with the use of pure vegetable oils as fuels in compression ignition (Diesel) engines are caused by high fuel viscosity. Transesterification of the oil with short-chain alcohols (such as methanol or ethanol) to corresponding fatty esters is the most promising solution to the high-viscosity problem. In this work, the transesterification method was applied to crude safflower seed oil of Turkish origin using methanol. The variables affecting the monoester yield, such as:

1. Molar ratio of alcohol to vegetable oil;
2. Reaction temperature; and
3. Type and amount of alkali catalyst used

were investigated. In the presence of 1.0 wt% KOH as the reaction catalyst, 97.7% ester yield was achieved within 18 min at a reaction temperature of 69 ± 1°C using 1:7 vegetable oil-alcohol molar ratio. A significant improvement was observed in viscosity and other physical properties with the ester product compared to the parent vegetable oil. ASTM fuel properties of the methyl ester product were in accordance with those obtained for commercial Grade No.2-D diesel fuel.

Index Entries: Safflower seed oil; viscosity; transesterification; methyl ester; fuel properties.

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INTRODUCTION

Supply–demand imbalances in the energy sector owing to constantly expanding populations and industrial growth, unreliable oil price policies that result in oil shortages, and energy crisis together with the predicted depletion of conventional fossil-derived fuels stimulated interest and research in the field of new renewable fuel alternatives. Among the new energy sources, biomass potential is particularly attractive compared to fossil resources since it has the advantage of being renewable. Liquid fuels are a vital necessity particularly for agricultural production, which largely depends on diesel fuel. Timing of the field operations, such as planting, cultivating, and harvesting, within a seasonal cycle is especially critical. To keep all of these energy-intensive operations on track, a dependable and readily available source of liquid fuel is essential; therefore, agriculture and farming sectors throughout the world are looking for ways of controlling their own liquid fuel supplies (*1–5*). In the developing countries whose agriculture-based economics are particularly vulnerable to fuel shortages, the need to become less dependent on oil imports and to ensure the continuation of agricultural activities with their own resources is even more important. A biomass-based technology is an alternative path to the energy development process in these countries and will eventually help to ease the burden of oil importation on their economies. As a source of biomass for producing liquid fuel, the majority of investigations have concentrated on vegetable oils and their derivatives since they seem to have the potential to be used as fuel alternatives for Diesel engines (*6,7*).

There are more than 350 oil-bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (*2*). The major problems associated with the use of vegetable oils in the compression ignition engines are caused by their high fuel viscosity, which is approx 10 times of that of Grade No.2-D diesel fuel. Dilution, microemulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. Among these techniques developed for reducing the high viscosity of vegetable oils, chemical conversion of the oil through transesterification with short-chain alcohols, such as methanol and ethanol, to its corresponding fatty ester appears to be the most promising solution (*8–12*).

Türkiye, like most of the developing countries of the world, has a vast agricultural potential, yet the country is highly dependent on oil imports and provides 90% of the crude oil demand through imports. An estimated increase of 73% in the country's oil crop production is expected in the near future with the completion of a major irrigation project in the Southeast Anatolia region (*13*). Therefore, the primary target of this study was to investigate the important parameters of the transesterification process for ester fuel production using an oil seed of minor importance for the edible oil industry in Türkiye, and provide a basis for the State Planning Department to consider and encourage the production of ester fuels within the scope of future agricultural development plans. Safflower is an oil seed that is cultivated in the Central Anatolia and Thrace regions of Türkiye within the scope of certain projects supported by the Ministry of Agriculture and Forestry. The crude oil extracted from a variety of safflower seed was transesterified using methanol, and the variables affecting the monoester yield were investigated. The ester fuel produced under the determined optimum conditions was tested and compared for its fuel properties with Grade No.2-D diesel fuel.

MATERIALS AND METHODS

Oil from the Yenice variety of safflower seed grown in the Thrace region of Türkiye was processed by mechanical cold-press extraction. The cruce oil obtained from Yenice safflower seed was filtered, but was not refined furthermore. The technological characteristics of the seed and the oil were determined according to standard methods of oil and fat analysis (*14,15*). Fatty acid composition of the oil was analyzed using United Technologies Packard Model 4337A gas chromatograph fitted with a hydrogen flame detector and a stainless-steel column (2 m × 5 mm) packed with 10% DEGS on Chromosorb W. The column temperature was 150–190°C, and flow rate of the carrier gas (nitrogen) was 25 mL/min. Fatty acid composition of the oil and technological characteristics of the seed and oil are given in Table 1.

After the characterization of the oil, the transesterification technique was applied using methanol. Reactions were performed in a 250-mL three-necked flask equipped with a reflux condenser and a contact thermometer. The free neck of the flask was used for taking samples from the reaction mixture at certain time intervals. Reaction mixtures were heated on a magnetic heater-stirrer to a few degrees below the boiling point of methanol, and reaction catalyst was added to the mixture at that moment. Reaction temperatures were controlled within a range of ±1°C. One-milliliter samples were withdrawn from the reaction mixture at certain time intervals. They were quenched in an equal volume of cold distilled water to instantly seize the reaction and were then centrifuged. Conversion of vegetable oil to its monoester was analyzed with Iatroscan TH-10 MK IV TLC/FID (thin-layer chromotography/flame ionization detector) Analyzer where the FID was operated with hydrogen and air flow rates of 160 and 2000 mL/min, respectively. Solutions to be analyzed were prepared by dissolving an appropriate portion of the oil layer in chloroform to give a concentration of 3.0 mg/mL. 1.6 μL of these solutions were applied to Type SIII Chromarods using the automatic Sample Spotter Model 3200/15-01. The rods were developed in glass tanks using a developing system

Table 1
Technological Characteristics of Yenice Safflower Seed and Oil

Seed characteristics		
Average weight (10^{-5} kg)		4.4
Average length (10^{-3} m)		7.4
Average husk content (wt%)		40.0
Moisture content (wt%)		7.7
Oil content (dry basis, wt%)		32.8
Fat characteristics		
Density @ 298 K (kg/m^3)		918.6
Refractive index @ 293 K		1.4763
Acid value (mg KOH/g)		2.90
Saponification value (mg KOH/g)		189.2
Iodine value		
Hanus method (g I_2/100g)		147.6
Wijs method (g I_2/100g)		144.3
Unsaponificable matter (wt%)		0.9
Fatty acid composition (wt%)		
Palmitic	16:0	7.12
Stearic	18:0	2.13
Oleic	18:1	12.07
Linoleic	18:2	77.07
Linolenic	18:3	1.61
Calculated mean mol wt of the oil (kg/mol kg)		854.7

of petroleum ether (bp 40–60°C), diethyl-ether, and acetic acid in volume ratios of 70:30:2, respectively, for 20 min. They were then kept at room temperature for 5 min and dried at 110°C in a ventilated oven for another 5-min period. Developed rods were placed in the frame of the Iatroscan Analyzer, and the signals produced were evaluated by a recorder-integrator system (Iatrocorder TC-11).

At the end of the reaction, the mixtures were allowed to cool to room temperature and taken into a separatory funnel where the ester and glycerol layers separated. The excess methanol in the ester layer was eliminated in a rotating evaporator under reduced pressure. The crude ester was then dissolved in petroleum ether, washed with water, acidified using glacial acetic acid until pH = 7 was reached, washed several times with water, dried over anhydrous sodium sulfate, and the petroleum ether was removed in the rotating evaporator under reduced pressure, hence revealing the refined methyl ester product.

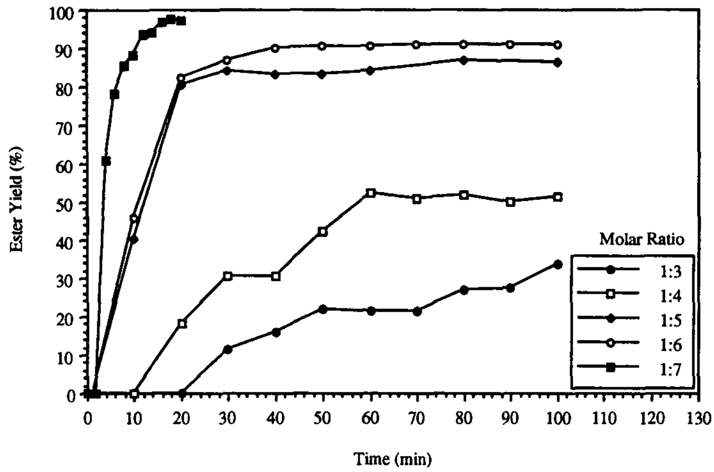

Fig. 1. Effect of vegetable oil-methanol molar ratio on ester yield.

RESULTS AND DISCUSSION

The variables affecting the monoester yield during transesterification reaction, such as the molar ratio of alcohol to vegetable oil, reaction temperature, and type and amount of alkali catalyst used, were investigated. Conversion of the triglyceride to monoester, di-, and monoglycerides was determined quantitatively by taking samples every 2 min from the reaction mixture and analyzing with the Iatroscan Analyzer. Considering the previous transesterification applications in the literature, Yenice safflower seed oil was transesterified at 1:3, 1:4, 1:5, 1:6, and 1:7 vegetable oil-methanol molar ratios using 1% by weight of oil potassium hydroxide as the reaction catalyst and keeping the reaction temperature slightly above the boiling point of methanol at 69 ± 1°C (*12,16–20*). The stoichiometry of transesterification reaction requires 3 mol of alcohol/mol triglyceride to produce 3 mol of fatty ester and 1 mol of glycerol. The ester yield results at various molar ratios (Fig. 1) showed the importance of using excess alcohol. Ester yield increased with the increase in the excess amount of alcohol, and at 1:7 safflower oil-methanol molar ratio, a methyl ester yield of 97.7 wt% was achieved within 18 min. Studies by several investigators also showed that excess amount of alcoholic component favors the yield of monoester product (*13,17,21–24*).

The effect of lower reaction temperatures on ester yield was investigated using 1:7 molar ratio and 1% potassium hydroxide as catalyst. Transesterification reactions were conducted at 49 ± 1°C, 59 ± 1°C, and 69

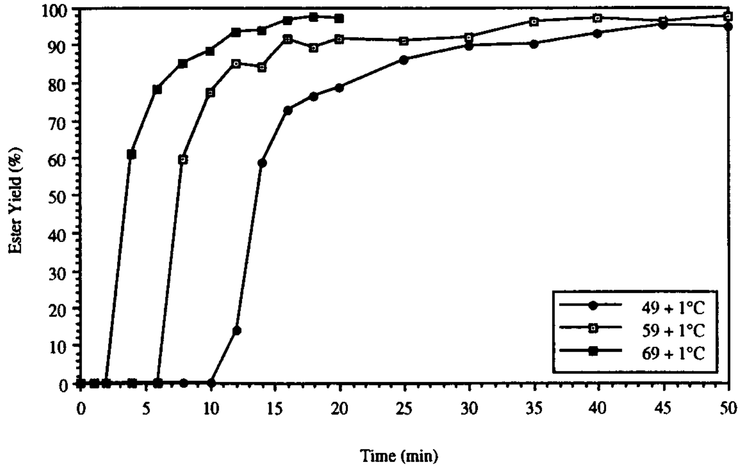

Fig. 2. Effect of reaction temperature on ester yield.

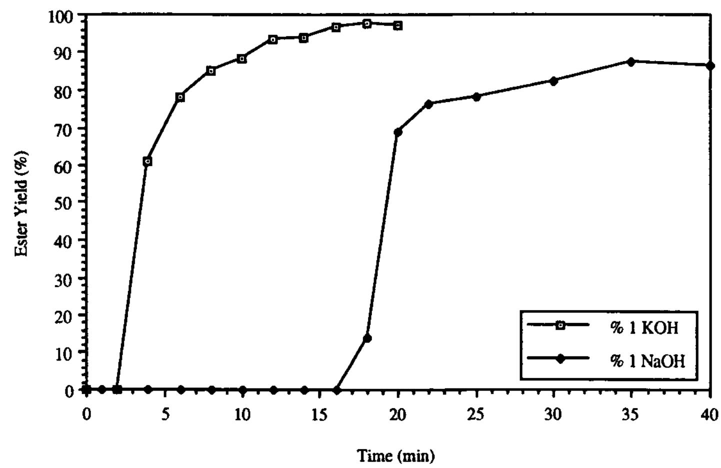

Fig. 3. Effect of alkali catalyst type on ester yield.

± 1°C. It was observed that increasing reaction temperature had a favorable influence on ester conversion (Fig. 2). Although at 69 ± 1°C, an ester yield of 97.7% was obtained in 18 min, at 59 ± 1°C, the same ester yield was achieved in 50 min. The conversion was much slower at 49 ± 1°C, and the yield was 95% at the end of 50 min.

Alkali-catalyzed transesterification is known to proceed much faster than acid-catalyzed transesterification (*13,17,19,25*). In order to compare the effects of two relatively low-cost alkali catalysts on the transesterification reaction, experiments were performed using the same amount (1 wt%) of potassium hydroxide and sodium hydroxide at 1:7 molar ratio and a reaction temperature of 69 ± 1°C. Ester yields obtained using potassium hydroxide and sodium hydroxide as catalysts are shown in Fig. 3.

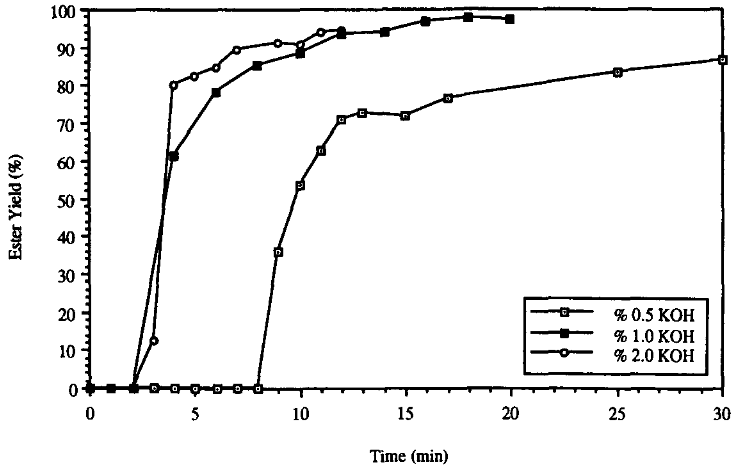

Fig. 4. Effect of the amount of alkali catalyst on ester yield.

The conversion was very slow with sodium hydroxide, and the ester yield was only 13.8% at the end of 18 min. However, potassium hydroxide was superior compared to sodium hydroxide and gave 97.7% ester yield in 18 min.

To determine the effect of the amount of alkali catalyst on ester yield, three separate experiments were performed using 0.5, 1, and 2% (by weight of oil) potassium hydroxide as catalyst at triglyceride:alcohol molar ratio of 1:7 and a reaction temperature of 69 ± 1°C. The effect of the amount of catalyst on ester yield is shown in Fig. 4. With 0.5% potassium hydroxide, the ester conversion was very slow, whereas with 2% potassium hydroxide, it was observed that all the triglyceride was converted at the end of 12 min and the methyl ester yield was 94.5% when the reaction was practically over. Therefore, 1% potassium hydroxide was considered to be the appropriate amount for the overall transesterification reaction.

The optimum conditions determined for the transesterification of crude safflower oil with methanol can be summarized as: 1:7 vegetable oil-alcohol molar ratio, 1 wt% potassium hydroxide catalyst, and 69 ± 1°C reaction temperature. Viscosity of the ester product obtained under the optimum conditions improved considerably as compared to that of the parent vegetable oil. Kinematic viscosity-temperature curves for Yenice safflower seed oil, Yenice safflower seed oil methyl ester, and Grade No.2-D diesel fuel are compared in Fig. 5. At 40°C, the kinematic viscosity value of safflower seed oil (29.4 cSt) was about 10 times higher than that of diesel fuel, whereas the viscosity value for methyl ester product (4.1 cSt) was only 1.3 times of that of reference Grade No.2-D diesel fuel. According to ASTM D 975-90 and ASTM D 445 diesel fuel specifications, kinematic viscosity of the methyl ester product was within the limits specified for Grade No.2-D diesel fuel. Methyl ester fuel was further tested for other fuel properties. Fuel properties of the methyl ester product and reference

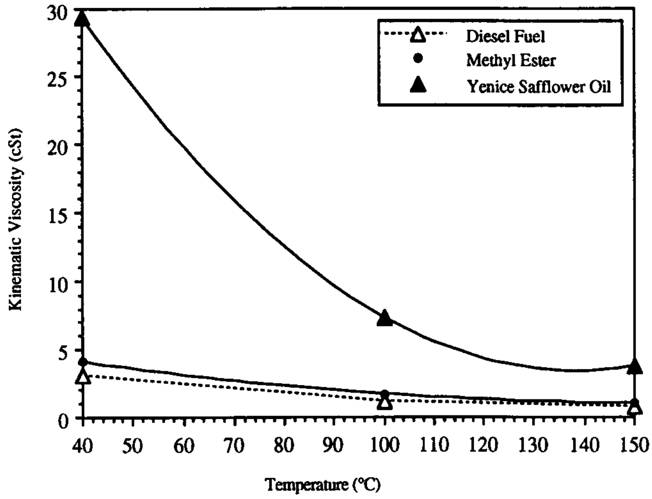

Fig. 5. Variation of viscosity with temperature for Yenice safflower oil, methyl ester and diesel fuel.

Table 2
ASTM Fuel Properties of Safflower Seel Oil
Methyl Ester and Grade No.2-D Diesel Fuel

Properties	Method	Grade No.2-D diesel fuel	Methyl ester
Relative density @ 15.56/15.56°C	D-4052	0.8616	0.8882
Refractive index @ 20°C	D-1218	1.4814	1.4595
Surface tension @ 25°C (mN/m)	D-971	27.6	30.7
Cetane number (measured)	D-613	42.9	49.8
Gross heating value (MJ/kg)	D-240	45.25	40.06
Flash point (°C)	D-92	—	180
	D-93	52	149
Pour point (°C)	D-97	−18	−6
Copper corrosion 3 h @ 100°C	D-130	1a	1a
Sulfur content (wt%)	D-4294	0.26	0.02

Grade No.2-D diesel fuel are given in Table 2. Comparison of the fuel properties and their evaluation according to ASTM D 975-90, the Standard Specification for Diesel Fuel Oils, indicated that Yenice safflower oil methyl ester had similar properties as Grade No.2-D diesel fuel.

CONCLUSIONS

In this study, transesterification, the most promising technique for modifying the high viscosity of vegetable oils, was investigated using crude Yenice safflower seed oil. Parameters affecting the methyl ester yield were tested in several steps, and 1:7 molar ratio of vegetable oil–methanol proved to be the appropriate ratio for transforming the oil to its methyl ester in the highest yield and in the shortest reaction period. One percent by weight of oil, potassium hydroxide was more effective as the reaction catalyst than an equal amount of sodium hydroxide. The trans-esterification of vegetable oils to fatty esters can successfully be performed with a high yield at mild reaction temperatures (69 ± 1°C) in 18 min. Methyl ester of transesterified Yenice safflower seed oil had significantly lower viscosity than that of the parent oil itself. Since high viscosity of the oil was the major obstacle for its use as a fuel alternative, this decrease in viscosity greatly reduces the concerns about its performance in the CI engine. The ASTM standard tests provided a significant insight into the potential of the methyl ester as a diesel fuel alternative. The fuel properties of safflower seed oil methyl ester were very close to those of Grade No.2-D diesel fuel, and therefore, it can be tested safely in any CI engine that is suitable for Grade No.2-D diesel fuel.

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