Evaluation of Turkish Sulphur Olive Oil as an Alternative Diesel Fuel

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Esterification of Turkish sulphur olive oil with different types of straight- and branched-chain monohydric alcohols has been investigated. Reaction conditions such as temperature and time have been evaluated, and monoester yield has been determined. As the alcohol component, direct application of an industrial by-product such as crude fuel oil has been investigated. Finally some preliminary laboratory tests concerning the suitability of the fuel oil monoester as a diesel fuel substitute have been performed.

Eighty five percent of the total world energy consumption is generated through oxidation of fossil fuels. Because the reserve of fossil fuels is somewhat limited, investigations concerning the renewable fuel alternatives are modern topics of technological development. Blends of diesel fuel with vegetable oils or direct application of vegetable oils as motor fuel alternatives are of potential importance (1,2). These alternatives show a number of problems, such as the higher viscosity of the material and the excessive carbonaceous deposits in the cylinders and on the injector nozzles of the engine. The technique of producing fatty acid monoesters by the alcoholysis of fatty oils is one suggested approach to obtain a motor fuel alternative. In earlier reports using soybean, winter rape, rapeseed and used frying oils, monoesters were prepared and their suitability as renewable diesel engine fuels was investigated (3–7).

MATERIALS AND METHODS

Sulphur olive oil is a rather low quality vegetable oil. It is obtained through a solvent extraction of olive press cake, a by-product of high quality olive oil manufactured for edible purposes. It is also called "Orujo oil" in Spain, and "Olive husk oil" or "Olive oil foots" in Anglo-American countries.

In Turkey sulphur olive oil has potential importance, because press cake produced in local rural mills is transferred to central plants, where a solvent extraction process is performed. During storage and transportation of these cakes, their oil content undergoes chemical alteration, due to enzymatic hydrolysis and atmospheric oxidation. Therefore, oil extracted from the press cake is different from the original edible olive oil and is suitable mostly for industrial purposes. For our experiments samples of sulphur olive oil have been provided from a local soap and glycerol manufacturing company, "Hacı Sakir Sabun ve Gliserin Fabrikası," in Istanbul. Commercial grade fuel oil, which is a by-product of the crude spirit refining process, has been obtained from the molasses alcohol fractionation unit of the state Beet Sugar Refinery in Eskisehir, central Anatolia. Pure alcohols used for the esterification of sulphur olive oil were all anhydrous, with the exception of commercial grade ethanol which was dehydrated through azeotropic distillation before use. The chemical characteristics of sulphur olive oil samples were determined according to usual standard methods of fat and oil analysis (8). For the determination of the refractive index an Abbe type refractometer was used. The viscosity and the density of the prepared samples were determined according to DIN 51561 and ASTM D 1217, respectively.

The fatty acid composition of the sulphur olive oil was determined using a Varian 3700 gas chromatograph fitted with a hydrogen flame detector and a stainless steel column (2 m × 5 mm) packed with 10% diethyleneglycol succinate on Chromosorb W(AW). The column temperature was adjusted to 180 C and the flow rate of the carrier gas, nitrogen, to 30 ml/min.

Taking into consideration the composition of sulphur olive oil, it was necessary to perform simultaneously the reactions of direct esterification and of alcoholysis under acidic conditions. For this purpose anhydrous alcohols such as methanol, ethanol, n-propanol, n-butanol, i-propanol and pure fermentation amyl alcohol were used as pure alcohol components. The "fermentation amyl alcohol" or commercial amyl alcohol is practically a natural blend of isoamyl and d-amyl alcohols in nearly equal proportion (b.p. 128–132 C). For the final esterification experiments a commercial grade fuel oil containing 12% water was used.

Intentionally no special purification was applied to this crude material; its main constituent is about 68.5% fermentation amyl alcohol isomers (nearly equal parts of isoamyl and d-amyl alcohols); beside the water content, the remainder consisted of a mixture of ethyl, n-propyl and isobutyl alcohols. An average molecular weight of 56.2 g/mol-g was estimated by calculation. Specific gravity was determined as 0.8360 g/ml at 20 C. As is known, with alkaline catalysts the reaction of alcoholysis is performed in a much shorter period of time. But if the oil component is a low grade material rich in free fatty acids such as sulphur olive oil, the alkaline type catalyst is deactivated. Therefore, the experiments were performed with the use of an acidic catalyst. For this purpose an approximate molar ratio of alcohol/oil = 30/1 was applied and as a catalyst 1%

TABLE I

Physical and Chemical Characteristics of Sulphur Olive Oil

Refractive index, n_D^{20}	1.4655
Density, at 20 C, g/ml	0.9087
Viscosity, at 20 C, cSt	68.53
Iodine value (Hanus)	80.28
Saponification value	193.53
Hydroxyl value	28.18
Dihydroxy compounds, weight %	5.75
Acid value	86.41
Ester value	107.12

TABLE 2

Fatty Acid Composition of Sulphur Olive Oil Used for the Experiments

Fatty acid constituents	weight %
Myristic	2.31
Palmitic	12.18
Stearic	2.16
Oleic	79.27
Linoleic	4.08

concentrated sulphuric acid was added to the reaction medium based on the weight of the oil component. All of the reactions were conducted near the boiling point temperature of the mixture. The reaction vessel was fitted with a reflux condenser and a vigorous mixing paddle. For the selection of these reaction conditions the report of Freedman et al. was considered (9).

In order to control the rate of esterification, the composition of samples taken during the reaction was determined by the use of thin layer chromatography (TLC) with silica gel G (10) and a solvent system of light petroleum:diethyl ether:acetic acid (75:25:1). The spots were visualized by direct action of iodine vapors.

The motor fuel characteristics of the esterified sulphur olive oil were determined according to ASTM test methods.

RESULTS AND DISCUSSION

The technological characteristics of sulphur olive oil sample which was used for the experiments are summarized in Table 1.

According to analysis performed by gas chromatography, the quantitative constituent fatty acid composition of the sulphur olive oil sample used for the experiments is shown in Table 2. The major component fatty acids contained in sulphur olive oil are palmitic, stearic, palmitoleic, oleic and linoleic acids. They are present partly as free acids and partly as mono-, di-and triglycerides. Based on the above data and estimating an average molecular weight of 277 g/mol-g for the component fatty acids, the following approximate composition of compounds present in sulphur olive oil has been calculated: 42.74% free acids, 5.75% monoglycerides, 10.7% diglycerides and 40.3% triglycerides. This composition corresponds to an approximately average molecular weight of sulphur oil 425 g/mol-g.

The reaction time of alcoholysis and esterification is dependent on the boiling point, carbon-number and the structure of the alcohol components. As the boiling points of branched chain alcohols are lower than those of straight chain alcohols, the reaction with branched chain alcohols took a much longer time.

As can be seen from Table 3, depending on the type of the single alcohol components a reaction time of 2–45 hr was necessary for formation of the respective esters; a yield of about 95 to 99 was attained. These results are in near agreement with those obtained by Freedman et al. (9).

A further series of experiments was performed with commercial grade fuel oil as the alcohol component; results are shown in Table 4. To obtain a yield of about 88% monoesters a reaction time of 20 hr was necessary; the reaction temperature did not raise above 97 C.

TABLE 3

Monoester Formation from Sulphur Olive Oil and Pure Alcohols

Alcohol component	Reaction temp, C	Reaction time, hr	Acid value of the monoesters	Saponification value of the monoesters	Monoester yield, %
Methanol	67	35	1.88	186.41	98.98
Ethanol	81	25	6.66	171.03	96.1
Propanol	101	20	2.26	183.00	98.77
Butanol	120	3	6.77	133.65	94.96
Fermentation amyl alcohol	122	2	4.52	155.63	97.09
i-Propanol	85	45	6.84	131.98	94.82

TABLE 4

Monoester Formation from Sulphur Olive Oil and Commercial Grade Fuel Oil

Reaction temp, C	Reaction time, hr	Acid value of the monoesters	Saponification value of the monoesters	Monoester yield, %
97	20	9.95	82.79	87.98
97	30	9.95	79.87	87.48
97	50	8.97	82.02	89.80

TABLE 5

Diesel Engine Fuel Properties of Sulphur Olive Oil/Fuel Oil Monoester and of its Blends with Standard Quality Diesel Oil

Tests performed	Guaranty specifications	Unblended diesel oil	Unblended monoester	Blended diesel oil with 10% monoester	Blended diesel oil with 20% monoester	Test methods
Color, ASTM	3 max	1–1.5	5–5.5	1.5–2	2–2.5	ASTM D 1500
Specific gravity, 15.6 C	0.820–0.850	0.8338	0.8436	0.8300	0.8358	ASTM D 1298
Flash point, C	55 min	63	44	48	44	ASTM D 93
Distillation 90%, C	357	338	292	345	345	ASTM D 86
Corrosion	No. 1 b max	No. 1 a	No. 1 a	No. 1 a	No. 1 a	ASTM D 130
Viscosity, 97.8 C, SSU	32–45	34.9	37.8	34.8	35.7	ASTM D 88
Pour point, C	-1.1 max	-3.3	-23	-6.6	-6.6	ASTM D 97
Ramsbottom carbon residue of the 10% distillation residue, weight %	0.25 max	0.09	0.43	0.05	0.14	ASTM D 524
Cetane number	50 min	57.5	20	58.5	58.5	ASTM D 976
Sulphur content, weight %	1.0 max	0.65	—	—	—	ASTM D 129
Ash content, weight %	0.01 max	Trace	Trace	Trace	Trace	ASTM D 482

Taking into consideration the reaction temperature and time, a higher yield of ester should be expected. But compared with the higher yields achieved with the fermentation amyl alcohol and with other anhydrous alcohols this lower yield of ester is probably due to the water content of the crude fuel oil (see Tables 3 and 4).

Preliminary tests concerning the motor fuel suitability of the monoester mixture based on commercial grade fuel oil as the alcohol component were performed according to the diesel fuel quality specifications of Tupras, Izmit Petroleum Refinery Inc., Izmit, Turkey, but due to the lack of suitable laboratory facilities no running engine tests were performed.

According to experimental data shown in Table 5, it can be suggested that a blend of monoesters obtained from sulphur olive oil and commercial grade fuel oil may prove itself as a useful diesel fuel alternative.

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