Esterification Reaction of Oleic Acid With a Fusel Oil Fraction for Production of Lubricating Oil

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ABSTRACT: In this study, the esterification of oleic acid with a fraction of fusel oil was investigated. The variables that affect ester yield, such as temperature, molar ratio of oleic acid to alcohol, and amount of catalyst, were determined. Powdered silica gel was chosen to remove water instead of granular silica gel, magnesium sulfate, or benzene. The behavior of amyl alcohols and the fusel oil fraction was compared. The esterification reaction was carried out under the reaction conditions selected as optimal, and the ester conversion of the reaction was 97.3%. The product mixture compressed products, excess reactants, catalyst, and desiccant. Oleate ester and oleic acid (2.7%) were obtained using the refinement steps of filtration, evaporation, washing with distilled water, and drying over sodium sulfate.

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KEY WORDS: Additive for lubricants, environmentally friendly lubricating oil, esterification, ester yield, fusel oil, lubricating oil, oleic acid, synthetic lubricating oil.

Basic oleochemicals that are derived principally from natural feedstocks are referred to as natural oleochemicals. Raw materials for most natural oleochemicals are tallow, tall oil, and vegetable oils. Basic oleochemical products may be classified as fatty acids, fatty alcohols, and glycerine. Industrially, most fatty acids are obtained directly from animal or vegetable sources, resulting in fatty acids with linear even-numbered carbon chains. The initial process for obtaining fatty acids from fats and oils is hydrolysis. It is possible to produce various industrial products from fatty acids. Among fatty acid products, fatty acid esters have important applications as solvents, plasticizers, resins, plastics, coatings, perfumes, flavors, cosmetics, soaps, medicinals, biofuels, and lubricants (1–3).

Esters are known as natural lubricating oils. Besides being used as lubricants like other ester types (diesters, trimelliate esters, C_{36} dimer acid esters, phthalate esters, and polyols), fatty acid esters can also be evaluated as synthetic lubricating oils.

Before the early 1800s, the main lubricants were natural esters contained in animal fats or in vegetable oils. During World War II, a range of synthetic lubricating oils was developed. Today, technology is available for high-quality synthetic lubricating oils.

Synthetic lubricating oils based on renewable sources are important in developing environmentally acceptable lubricating oil alternatives. The use of environmentally acceptable vegetable oil-based product as lubricants has many advantages. They are nontoxic, biodegradable, derive from renewable resource, and have a reasonable cost when compared to other synthetic fluids.

In this study, the esterification product of oleic acid with a fraction of molasses fusel oil was investigated as a lubricating oil candidate. Molasses fusel oil, a by-product of the fermentation process of industrial ethanol production, is an alcohol mixture having a boiling point range of 80–132°C. Oleic acid is generally considered to be the predominant fatty acid in nature. It constitutes 50% or more of the total acids of many fats; few fats are known to contain less than 10% of this acid (4). The esters of oleic acid and different types of alcohols can be used as a lubricating oil. In this study, the esterification product of oleic acid and a fraction of fusel oil was presented as a lubricating oil for the first time.

EXPERIMENTAL PROCEDURES

The oleic acid was obtained from Mert Chemicals Co. (Istanbul, Turkey). The physical and chemical characteristics of the oleic acid, which were determined according to the standard methods of oil and fat analysis were as follows: density (20°C), 891.6; refractive index (20°C), 1.4597; acid value, 207.6 mg KOH/g; saponification value, 200.6 mg KOH/g; iodine value, 79.5 g I/100 g; water content, 0.08 vol%; fatty acid composition (wt%), caprylic acid, 0.08; capric acid, 0.14; lauric acid, 1.35; myristic acid, 1.36; palmitic acid, 6.32; stearic acid, 1.44; oleic acid, 88.74; arachidic acid, 0.38; gadoleic acid, 0.19; calculated mean molecular weight of oleic acid, 278.9.

Fusel oil used in the experiments was obtained from Turkish Sugar Factories Inc. (Eskişehir, Turkey). It had a high (8.6% vol/vol) water content, and its density at 20°C was 853.6 kg/m^3. Because of the high water content of the fusel oil, the completion of the reaction would be affected negatively. Therefore, fusel oil was distilled according to the results of Karaosmanoğlu *et al*. (5), and the higher boiling fraction [above 120°C and 75% (vol/vol) fusel oil] of fusel oil containing 0.1% (vol/vol) water was used as the esterification reactant in the experiments. The composition of the fusel oil fraction was as follows: ethanol, 0.06 wt%; 1-propanol, 0.41;

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1-butanol, 13.03; amyl alcohols, 86.50. Other reagents used in experiments were analytic-grade Carlo Erba (Milan, Italy) products.

The reactions were performed in a 250-mL three-necked flask equipped with a reflux condenser, a contact thermometer (ETS-D2 IKA-TRON; IKA Labortechnik, Dortmund, Germany), and a conventional thermometer. The reaction mixture was heated on a magnetic heater and stirrer (IKAMAG REC-G; IKA Labor Technik) until it reached the experiment temperature; catalyst (sulfuric acid) and desiccant (silica gel) were added to the mixture at that moment. The reaction temperatures were held constant within a range of ±1°C, and the thermometer neck was used for taking samples from the reaction mixture for chromatographic analysis at certain time intervals [to determine ester conversion (conversion of oleic acid to esters) percentages]. The samples were analyzed with Iatroscan TH-10 MK IV (Iatron Lab. Inc., Tokyo, Japan) thin-layer chromatography/flame-ionization detection (TLC/FID). One-milliliter samples for TLC/FID analysis were taken from the reaction mixture at certain time intervals, placed in test tubes, and reactions were quenched by setting the test tubes in an ice-filled vessel. Anhydrous sodium sulfate was added to the samples and then the samples were centrifuged. The anhydrous esterification product mixture was analyzed by TLC/FID.

After the reaction under conditions selected as optimal, the flask was allowed to cool to room temperature. The mixture was filtered to remove the silica gel from the product. Excess fusel oil fraction in the mixture was removed in a rotary evaporator under reduced pressure. The mixture was washed repeatedly with distilled water (30°C) until all the catalyst was removed. In order to observe the removal of the catalyst, a few drops of methyl red was added to the mixture. After removal of sulfuric acid, the acid number of the ester product was determined. The acid number was equal to the amount of oleic acid in the product mixture after the esterification reaction.

RESULTS AND DISCUSSION

The esterification reaction of oleic acid with the fusel oil fraction occurs as follows:

$$\text{oleic acid + fraction of fusel oil} \rightleftharpoons \text{oleate esters + water} \qquad [1]$$

In this reversible reaction, the molar ratio of reactants, temperature, catalyst, and removal of product from the reaction mixture are the variables affecting the conversion and the reaction rate.

Determination of removal of water for the esterification reaction of oleic acid–fusel oil fraction. Special methods are necessary to remove the water of esterification to shift reaction toward completion. Removal can be done with a solvent to form an azeotropic mixture with water according to the boiling points of alcohol and ester. The use of steam or inert gas to carry off the water formed in the esterification has also been suggested for completing the reaction. In addition, desiccants have been used to remove the water (6,7). In this study, benzene was added to form an azeotropic mixture in order to remove water magnesium sulfate, powdered silica gel, and granular silica gel were used as desiccants at the same reaction conditions. The ester conversions of every reaction were investigated and compared with each other. Initial esterification reaction conditions were chosen according to the study by Aksoy *et al.* (8): duration, 2 h; temperature, 90°C; acid/alcohol molar ratio, 1:1; and catalyst, sulfuric acid. In the experiment in which benzene was used, a water trap was added to the experimental equipment. In the experiments where desiccants were used, magnesium sulfate was previously dried at 110°C, and the silica gels at 180°C. These desiccants were used at 50% of the weight of the acid. Reactions carried out with this weight of desiccant had no problems in mixing, and high conversions were reached. Because of this, the effect of varying the amount of desiccant on the esterification conversion was not investigated. The comparison of ester conversions is shown in Table 1. The highest conversion was observed in the experiment with benzene. Conversions in the experiments with magnesium sulfate and powdered silica gel were similar, whereas the conversion in the presence of powdered silica gel was higher than with granular silica gel because of the higher surface area of the former.

In the experiments with magnesium sulfate, taking samples was hard because the pipette was plugged and the end mixture seemed to be turbid. Turbidity was not observed in the experiments with silica gels. The experiment with benzene also was carried out without any problem, as all chemicals were liquid, and a very high conversion was obtained. But, benzene is a fossil fuel-based and environmentally unacceptable chemical. Because benzene is acceptable, and because silica gel is a natural reactant, powdered silica gel was chosen to remove water in all subsequent experiments.

The effect of temperature on the esterification reaction of oleic acid with the fusel oil fraction. The equimolar mixture of oleic acid and fusel oil fraction boiled at 90°C. After the addition of catalyst and the desiccant to the mixture, it formed a heterogeneous mixture. The behavior of the mixture consisting of oleic acid, fusel oil fraction, sulfuric acid, and silica gel was investigated to determine maximum reaction temperature, which was 110°C. The reactions were carried out at 100, 90, 80, and 70°C with the aim of observing the effect of temperature decrease on the ester conversion. The other reaction conditions were as follows: duration, 2 hr; acid/alcohol molar ratio, 1:1; type of catalyst, sulfuric acid; amount of catalyst, 1% of the weight of the acid.

TABLE 1
Comparison of the Esterification Conversions in Reactions Using Various Desiccants and an Azeotrope

	Ester conversion (wt%)			
Duration (min)	Benzene	Magnesium sulfate	Silica gel powder	Silica gel granules
60	95.4	86.9	89.5	70.0
90	95.5	91.7	91.8	72.4
120	95.6	91.9	91.9	74.8

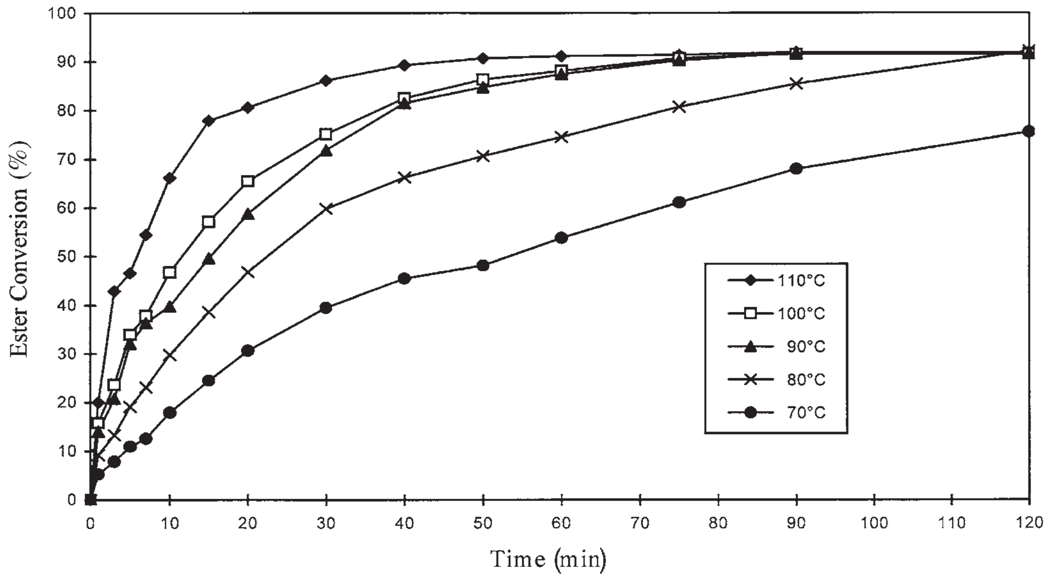

FIG. 1. Comparison of ester conversions of reactions carried out at different temperatures.

Ester conversions at the different temperatures are shown in Figure 1. Both temperature and duration affected the color of the product mixture. At the beginning, the mixture was yellow, but after the addition of the catalyst, it became orange, then brown, and at the end of experiment, black. In the experiment carried out at 110°C, the color became black at 20 min, while at 100°C at 40 min, at 90°C at 60 min, at 80°C in 70 min. The ester conversions at 60 min at 110, 100, 90, 80, and 70°C were 91.1, 88.1, 87.5, 74.6, and 53.8% respectively. After 90 min, the ester conversions were 91.9, 91.8, 91.7, 85.4, and 68.1%, respectively. That is, the ester conversions in experiments at 100 and 90°C were almost the same after 40 min. Hence, 90°C was found to be the most suitable reaction temperature because of the ester conversion and consumption of energy.

The effect of the molar ratio of reactants to the esterification reaction of oleic acid–fusel oil fraction. Among the variables affecting the ester yield in the esterification reaction, the most important one is the molar ratio of the reactants. Since the reaction is reversible, an increase in the amount of one of the reactants will result in higher ester yields. In order to determine the effect of molar ratio, oleic acid was esterified at molar ratios of 1:1, 1:2, 1:3, and 2:1 oleic acid/fusel oil fraction under the following conditions: duration, 2 h; temperature, 90°C; type of catalyst, sulfuric acid; amount of catalyst, 1% of the weight of the acid. The results at the three

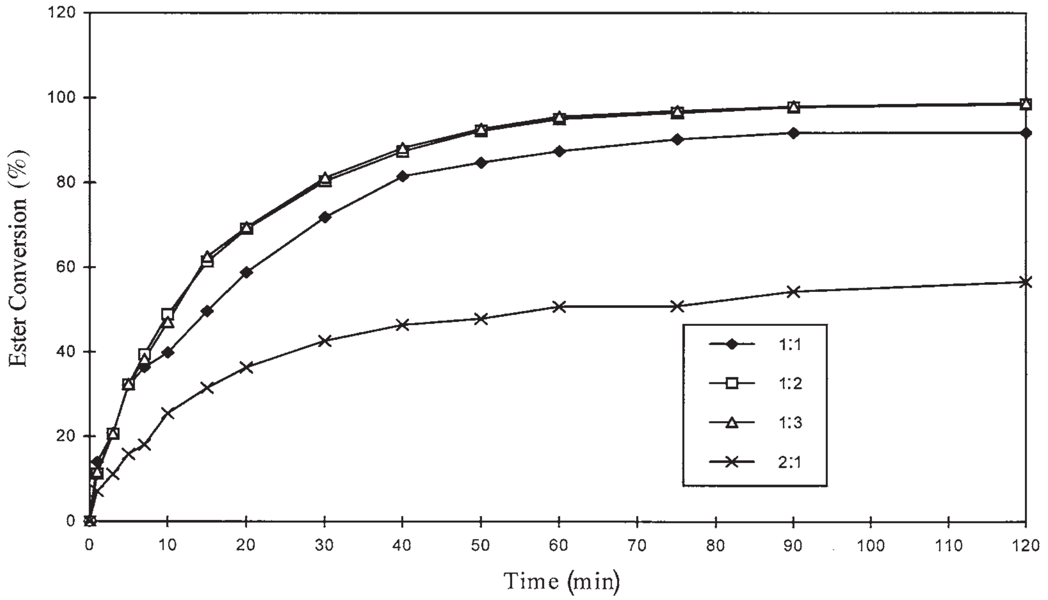

FIG. 2. Comparison of ester conversion for reactions carried out at different oleic acid/fusel oil fraction molar ratios.

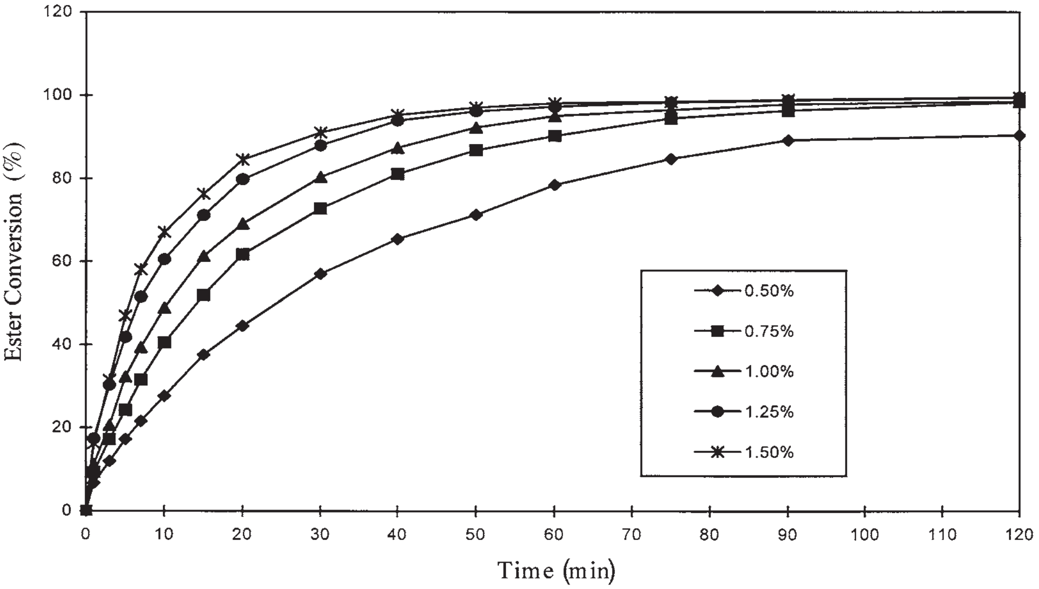

FIG. 3. Comprison of ester conversion of reactions carried out at different amounts of catalyst as a percentage of the weight of oleic acid.

molar ratios and 1:1 acid/alcohol molar ratio are shown in Figure 2.

As expected, a higher ester conversion was obtained in a shorter period of time for 1:2 and 1:3 molar ratios compared to 1:1. After 120 min, the ester conversion obtained in the reaction with the molar ratio of 2:1 was 56.6% (vs. a theoretical maximum of 50% if the moles of alcohol in the complex fusel oil fraction were exactly half those of oleic acid). After 50 min, the ester conversions were 90% at 1:2 and 1:3 molar ratios. After 90 min, both ester conversions were over 97% and nearly the same. At a 1:2 molar ratio, the mixture was orange at the end of 60 min and brown at the end of the experiment. The end mixture was light yellow in the reaction with the 1:3 molar ratio. After adding the catalyst, the mixture was black in the experiment carried out at a 2:1 molar ratio. The temperature and the amount of alcohol affected the color of the product mixture. Hence, 1:2 was found to be the most suitable molar ratio of oleic acid/fusel oil fraction.

The effect of the amount of catalyst on the esterification reaction of oleic acid–fusel oil fraction. To determine the effect of the amount of catalyst, experiments were carried out with 0.5, 0.75, 1, 1.25, and 1.5% catalyst as a percentage of the weight of the oleic acid (Fig. 3). The other reaction conditions were as follows: duration, 2 h; temperature, 90°C; acid/alcohol molar ratio, 1:2; type of catalyst, sulfuric acid. As the amount of the catalyst was increased from 0.5 to 1.5%, the near maximal conversion was reached in a shorter time. In the reaction where 0.5% of the weight of the acid as catalyst was utilized, ester conversion was 90.4% at the end of 120 min. In all amounts, the conversions rose quickly in the first 20 min; at the end of 120 min, they were nearly complete except for the reaction where 0.5% of the acid weight was used as catalyst. The color was light orange at 0.5%, dark orange at 0.75%, light brown at 1%, brown at 1.25%, and dark brown at 1.5%. Thus, the amount of catalyst affected the color of the ester product. After 60 min, the conversions for 1.25 and 1.5% catalyst were similar. The reaction where 1.25% of the weight of the acid was used as catalyst, was found to be the appropriate amount for the reaction. After 60 min, the ester conversion at 1.25% catalyst was 97.3%. Hence the reaction duration chosen was 60 min. After 60 min, the product mixture content was 97.3% oleate esters and 2.7% oleic acid.

Upon completion of all the experiments between oleic acid and fusel oil fraction, the optimal reaction conditions were determined to be as follows: duration, 1 h; temperature; 90°C; acid/alcohol molar ratio, 1:2; type of catalyst, sulfuric acid; amount of catalyst, 1.25% of the weight of the acid; desiccant, silica gel (powder); amount of desiccant, 50% of the weight of the acid.

The comparison of fusel oil fraction and amyl alcohols in the esterification reaction. The behavior of the fusel oil fraction was compared to the behavior of *n*-amyl alcohol and isoamyl alcohol under selected reaction conditions. The comparison of ester conversion of the fusel oil fraction and amyl alcohols is shown in Figure 4. Amyl alcohols performed better than the fusel oil fraction in the first 30 min. But after 50 min, all of them gave the same conversions. In comparing the alcohols, the conversion of *n*-amyl alcohol slightly exceeded that of isoamyl alcohol. That means branching decreases the ester conversion.

The refinement of the ester product. The product mixture was composed of esters of the alcohols of fusel oil fraction, unreacted oleic acid, excess of fusel oil fraction, sulfuric acid, and silica gel. To obtain pure ester product, the product mixture was refined to remove all the compounds from the mixture except oleic acid. As mentioned before, oleic acid can be

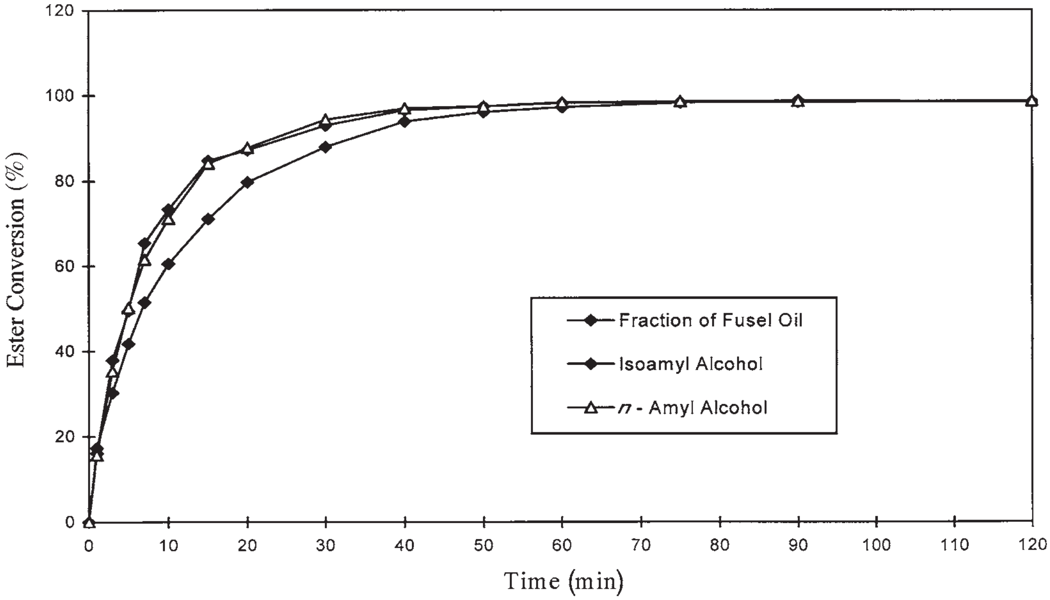

FIG. 4. Comparison of the ester conversion of reactions using the fusel oil fraction and amyl alcohols.

used as an additive for lubricants. Therefore oleic acid was not removed from the ester product. The end product after refining comprised 97.3% ester and 2.7% oleic acid.

REFERENCES

1. Kaufmann, A.J., and R.J. Ruebusch, Oleochemicals—A Look at World Trends, *INFORM 1*:1034–1048 (1990).
2. Hammond, E.G., The Raw Materials of the Fats and Oils Industry, in *Introduction to Fats and Oils Technology*, edited by P.J. Wan, American Oil Chemists' Society, Champaign, 1991, pp. 1–15.
3. Sonntag, N.O.V., Fat Splitting, Esterification, and Interesterification, in *Bailey's Industrial Oil and Fat Products,* edited by D. Swern, 4th edn., Interscience Publishers Division of John Wiley & Sons, New York, 1979, Vol. 2, pp. 113–127.
4. Markley, K.S., Nomenclature, Classification, and Description of Individual Acids, in *Fatty Acids: Their Chemistry, Properties, Production and Uses*, edited by K.S. Markley and Robert E. Krieger, Malabar, FL, 1983, Part 1, pp. 34–213.
5. Karaosmanoğlu, F., A. Işigigür, and H.A. Aksoy, Effects of a New Blending Agent on Ethanol–Gasoline Fuels, *Energy Fuels 10*:816–820 (1996).
6. *Kirk-Othmer Encyclopaedia of Chemical Technology*, 2nd edn., Interscience Publishers Division of John Wiley & Sons, New York, 1965, Vol. 8, pp. 313–356.
7. Markley, K.S., Esters and Esterification, in *Fatty Acids: Their Chemistry, Properties, Production and Uses*, edited by K.S. Markley and Robert E. Krieger, Malabar, FL, 1983, Part 2, pp. 758–773.
8. Aksoy, H.A., I. Kahraman, F. Karaosmanoğlu, and H. Civelekoğlu, Evaluation of Sulfur Olive Oil as an Alternative Diesel Oil, *JAOCS 65*:936–938 (1988).

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