Screening Vegetable Oil Alcohol Esters as Fuel Lubricity Enhancers

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ABSTRACT: Methyl and ethyl monoalkyl esters of various vegetable oils were produced for determining the effects of type of alcohol and fatty acid profile of the vegetable oil on the lubricity of the ester. Four methyl esters and six ethyl esters were analyzed for wear properties using the American Society for Testing and Materials method D 6079, Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig. Ethyl esters showed noticeable improvement compared to methyl esters in the wear properties of each ester tested. No correlation was found between lubricity improvement and fatty acid profile of the ester, except that esters of castor oil had improved lubricity over other oils with similar carbon chain-length (C_{18}) fatty acids.

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Biodiesel ester fuels have been examined as an alternative to petroleum fuels and as an additive to improve the lubricity of these fuels. Previously tested biodiesel ester fuel samples have given improved lubricity test results, but attention was not focused on the vegetable oil from which the fuel was derived (1). Each vegetable oil (and even specific varieties) has a characteristic fatty acid content profile. High-erucic acid rapeseed (HEAR) is raised as an industrial oil crop and is not an edible vegetable oil. One of the industrial uses of HEAR and its esters is as a component in specialty lubricants. Testing the ester of an oil with a known fatty acid profile would help determine if the fatty acid profile influences lubricity characteristics of its ester. Additionally, using ethanol or methanol as the alcohol in the esterification reaction would help in analyzing the effects of the type of alcohol on improving lubricity of the ester.

The U.S. Army has adopted a Single Fuel Forward policy, in which aviation-grade turbine-engine fuel (JP-8) (2) is used in Army ground vehicles and equipment. The fuel lubricity of many JP-8 fuels and some low-sulfur diesel fuels is not adequate to provide wear protection for some ground equipment fuel injection pumps (3). The JP-8 specification contains the Standard Ball-on-Cylinder Lubricity Evaluator (BOCLE) ASTM D5001 lubricity test. Passing this test does not guarantee acceptable fuel lubricity for ground application fuel system components. The high-frequency reciprocating rig (HFRR) test was developed to predict lubricity of fuels intended for ground equipment (4). Generally, a maximum wear scar of 450 µm in the HFRR test indicates acceptable fuel lubricity (5). The objective of this project was to define the lubricity improvement of JP-8 fuel that was imparted by biodiesel ester fuel samples prepared with varying chemical compositions.

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MATERIALS AND METHODS

Transesterification reaction. The monoalkyl esters were made by a transesterification reaction carried out at room temperature and atmospheric pressure in approximately 2500-mL batches. Sodium methoxide or sodium ethoxide (depending on the alcohol being used) was used as a catalyst at a concentration of 0.75% sodium by weight of triglyceride. To shift the reaction toward monoalkyl esters, 100% excess alcohol (6 mol) was used to obtain high (88–92%) conversions of oil into ester. The unpurified ester was then decanted off the top and subsequently purified by a patented two-stage extraction process with fresh glycerine (certified A.C.S. 99.7%; Fisher Scientific, Fairlawn, NJ) (6). The glycerine extraction/purification process was chosen in order to reduce the moisture content of the final product. Traditional water washing leaves a high Karl Fischer moisture content in the ester, which creates corrosion problems and hence is unacceptable for military applications.

Materials. The vegetable oils used in the transesterification reaction were soy (generic brand salad oil labeled 100% soy oil, bulk restaurant carboy from local wholesale grocery store, Clarkston, WA), Sterling rapeseed (local farm 1998 crop grown under contract to Idaho TransTech, Inc., Moscow, ID, custom crushed by Montana Specialty Mills, Great Falls, MT), Dwarf Essex rapeseed (local farm 1997 crop, custom crushed by University of Idaho Agricultural Engineering Dept., Moscow, ID), coconut (generic brand popcorn oil labeled 100% coconut oil, bulk restaurant carboy from local wholesale grocery store, Clarkston, WA), castor (bulk tank truck sample of #1 castor oil donated by Lifelast, Inc., Vancouver, WA), and partially hydrogenated canola (demonstration sample from French fry potato processor discontinued pilot test run donated by Idaho TransTech, Inc., Moscow, ID). The two different types of alcohol used were ethanol (USP absolute-200 proof, AAPER Alcohol & Chemical Co., Shelbyville, KY) and methanol (certified A.C.S. 99.9%, Fisher Scientific). All esters were made using elemental Na (lump 99%, aldrich Chemical Co., Milwaukee, WI) reacted with al-

TABLE 1
JP-8 Base Fuel Properties[a]

Property	Method[b]	JP-8 AL-24666[c]	MIL-DTL-83133E requirements[d]
API gravity (60°F)	D 1298	47.9	37–51
Density (15°C, kg/L)	D 12980	0.7884	0.775–0.840
Flash point (°C)	D 93	48	38 minimum
Freeze point (°C)	D 2386	–61.5	–47 maximum
Color	D 1500	<0.5	Report
Hydrogen (mass %)	D 5291	14.23	13.4 minimum
Net heat of combustion (MJ/kg)	D 240	43.2	42.8 minimum
Total acid number (mg/g KOH)	D 664	0.01	0.015 maximum
Sulfur (mass %)	D 4294	0.07	0.30 maximum
HFRR (mm)	D 6079	0.770	Not required
Scuffing load wear test (g)	D 6078	2100	Not required
Distillation (°C for percentage off)	D 86		
Initial		165	Report
10%		173	205 maximum
20%		175	Report
50%		181	Report
90%		192	Report
End point		206	300 maximum

[a]JP-8 fuel, aviation-grade turbine engine fuel; API, the density-reporting units specified by the military fuel specification; HFRR, high-frequency reciprocating rig.
[b]All methods from American Society for Testing and Materials (8).
[c]Sample provided by Southwest Research Institute, San ANtonio, TX.
[d]Reference 2; Report = report to customer, no required range.

cohol to form sodium methoxide or sodium ethoxide as the catalyst in the respective alcohol solution. Southwest Research Institute (SwRI; San Antionio, TX) sample AL-24666 of military grade aviation fuel JP-8, whose properties are shown in Table 1, was used as the blending agent.

Analytical methods. Lubricity testing was done according to the HFRR (60°C) method D 6079 (8) with additions of monoalkyl esters of biodiesel at 0.1, 0.5, and 1.0% by volume to JP-8 fuel. Fuel blends containing biodiesel were evaluated by the HFRR lubricity test to determine if the biodiesel ester fuel additive gave improved lubricity to the fuel.

The HFRR (PCS Instruments, London, England) uses an electromagnetic vibrator that oscillates a moving specimen against a fixed specimen immersed in the test fuel over a small amplitude (7). The HFRR standard operating conditions are as follows (8,9): fluid volume (mL), 2; applied load (kg), 0.2; speed (Hz), 50; duration (min), 75; fluid temperature (°C), 25 or 60; stroke (mm), 1.0; bath surface area (cm^2), 6; repeatability (mm), 0.062; reproducibility (mm), 0.127. The HFRR data reported are the means of two or three test runs. The test repeatability standard is 0.080 mm, and the operator runs at least two tests to determine if they repeat within 0.080 mm; if not, then a third test is run.

Kinematic viscosity measurements were made according to ASTM D 445 (8). Gas chromatography was used to determine the ester fatty acid profile, free glycerine content, and free alcohol content. The fatty acid profile was determined by using an HP5890 Series II gas chromatograph with an HP 7673 autosampler (Hewlett-Packard Co., San Fernando, CA), flame-ionization detector, and a 0.25 mm × 30 m, 0.25 μm film thickness DB-23 capillary column (J&W Scientific, Folsom, CA). The free glycerine content and free alcohol content were also determined using the HP5890 gas chromatograph and autosampler, but with a 0.25 mm × 30 m DB-1 capillary column (J&W Scientific). The free glycerine method was adapted from one published by the Research Institute for Chemistry and Technology of Petroleum Products (10). The free alcohol content was determined by spiking a sample with a known amount of alcohol to calibrate the analysis method.

RESULTS AND DISCUSSION

Fatty acid profile. The results of the fatty acid profile analyses are given in Table 2. The variety in the number of carbons

TABLE 2
Fatty Acid Profiles of Ester Given in Weight Percentage of Ester

Ester	Fatty acid[a]								
	Caprylic (8:0)	Capric (10:0)	Lauric (12:0)	Myristic (14:0)	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Coconut ethyl	7.23	5.72	46.03	18.57	9.54	2.99	7.38	2.32	—
Soy methyl	—	—	—	—	10.66	4.44	23.57	52.25	7.03
Soy ethyl	—	—	—	—	10.50	4.36	23.15	52.16	7.12
	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Ricinoleic (18:0)(–OH)	Arachidic (20:0)	Arachidonic (20:1)	Erucic (22:1)
Canola[b] ethyl	4.93	3.90	82.01	4.72	0.58	—	—	0.95	0.20
Sterling[c] methyl	3.22	1.33	17.75	12.79	5.74	—-	0.96	9.91	42.74
Sterling[c] ethyl	3.27	1.33	17.87	12.96	5.90	—	0.96	9.86	42.41
Dwarf Essex[c] methyl	2.70	0.98	13.69	10.77	7.08	—	0.81	7.37	50.95
Dwarf Essex[c] ethyl	2.72	1.02	13.75	10.84	7.12	—	0.84	7.34	50.63
Castor methyl	1.15	1.17	4.24	5.26	0.55	87.19	—	0.40	—
Castor ethyl	1.14	1.17	3.68	5.26	0.55	87.19	—	0.43	—

[a]Fatty acid (# carbon: # double bonds).
[b]From partially hydrogenated canola oil.
[c]From high-erucic acid rapeseed varieties.

TABLE 3
Other Physical Characteristics

Ester	Free glycerine[a] (wt%)	Kinematic[b] viscosity (cSt)	Alcohol content (wt%)
Coconut ethyl	0.07	2.91	0.12
Soy methyl	0.04	4.55	ND
Soy ethyl	0.04	4.46	ND
Canola ethyl	0.07	5.46	0.15
Sterling methyl	0.03	5.72	ND
Sterling ethyl	0.06	6.01	0.25
Dwarf Essex methyl	0.04	6.22	ND
Dwarf Essex ethyl	0.03	6.48	0.07
Castor methyl	1.21	12.69	0.95
Castor ethyl	1.10	17.63	2.32

[a]Method modified from Reference 10.
[b]Measurements made according to ASTM D 445.

in the carbon chain of each fatty acid is easy to see, as is the number of double and OH bonds. Another important feature to note is the similarity in the profiles between the methyl and ethyl esters of the same vegetable oil. This showed that the alcohol did not affect the fatty acid profile of the ester, so the influence of the profile and alcohol type could be separated and evaluated independently.

Free glycerine content. Free glycerine was low in most samples (Table 3). For all samples except castor, the mean of 0.05% was very close to the 0.03% lower detectable limit of the analytical procedure. This may have caused some error because the amount of free glycerine in the sample was so close to the end of the detectable range. Although 0.05% free glycerine is above the 0.02% ASTM PS 121-99 provisional biodiesel specification (8), when the esters are blended at 1% or less in JP-8 the resulting free glycerine level is significantly below the biodiesel specification, and the military specification has no glycerine limit. The free glycerine concentrations in the castor esters were roughly 23 times higher, with a mean of 1.16%. The castor esters also had a much higher viscosity.

Kinematic viscosity. As with the free glycerine analysis, all samples were within a kinematic viscosity range of 3–6 cSt except for the castor samples (Table 3). They were higher, but this time only by a factor of about 3. This difference in kinematic viscosity and free glycerine content led to treating the esters of castor oil as a separate subset as described in the section on lubricity testing.

Free alcohol content. The free alcohol contents of the methyl esters were all undetectable (below 0.03%) except for the castor methyl ester at 0.95% (Table 3). The ethyl esters ranged from 0.07% in the Dwarf Essex ethyl ester to 2.32% in the castor ethyl ester. All of these values except castor were also near the lower detectable limits of the testing procedure used, as in the free glycerine analysis.

Lubricity testing. The results of the lubricity tests were analyzed by dividing the test population into three different subsets. The first subset was the castor oil. Castor oil has a unique OH group in the middle of the 18-carbon chain of ricinoleic acid, which amounts to approximately 90% of the fatty acid profile (Table 2). Owing to this difference in chemical structure and to the increased free glycerine contents of these samples, it was decided to treat castor oil as its own subset. The second subset was the methyl esters, and the third was the ethyl esters.

In all cases, the lubricity of the sample tested improved with increasing volume of ester additive (Fig. 1), where the declining wear from 0.1 to 0.5% ester additive was clearly seen. The same trend continued with the lowest wear at 1.0%. In the case of 0.1% ester additive, there was no statistical difference in the lubricity of any subset compared to variations in the pure JP-8 turbine fuel. When all 0.1% ester samples were used in the determination of the statistical parameters, the results showed a normal distribution (Fig. 2). At two stan-

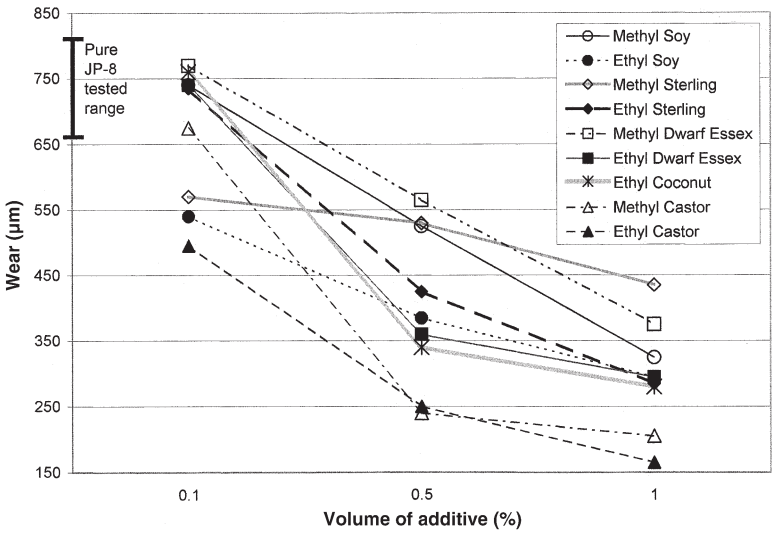

FIG. 1. Wear in the presence of each ester as a function of the percentage by volume of additive. Wear was determined by means of a high-frequency reciprocating rig. The identification of vegetable oils and their sources is presented in the Materials and Methods section.

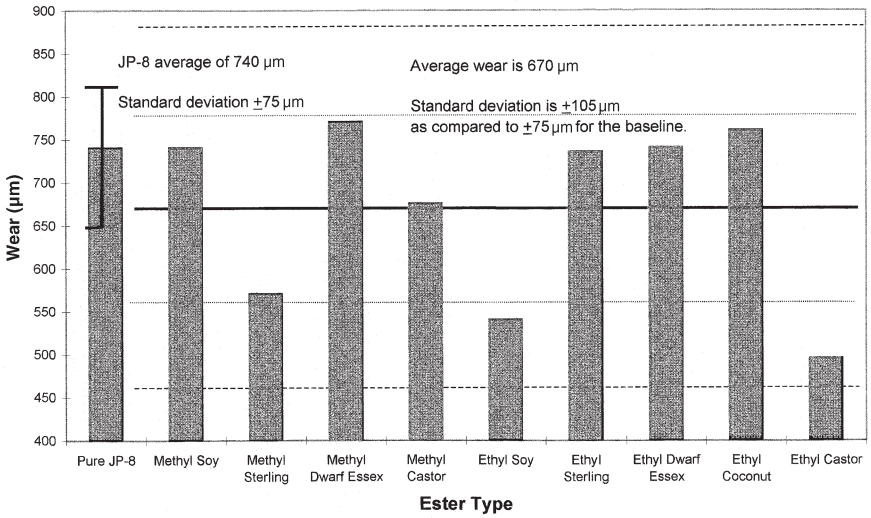

FIG. 2. Wear at 0.1% volume addition of ester. Bold line at 670 µm represents the mean, dotted lines are at ±1 standard deviation from the mean, and dashed lines are at ±2 standard deviations from the mean.

dard deviations, all samples were accounted for. This indicates that at 95% confidence there was no statistical difference between any of the samples. Although the average lubricity was slightly enhanced by adding 0.1% ester, there was no significant difference as to which type of ester sample was used.

Figure 3 shows the results of the lubricity testing for 0.5% ester additive where subsets 2 and 3, the methyl and ethyl esters excluding the castor oil samples, were evaluated. With the population separated into these subsets it was easy to analyze the hypothesis of increased lubricity for the ethyl esters as opposed to the methyl esters. In both cases the standard deviation of the subset was less than the standard deviation of the baseline measurements of 74.4 µm. The data within each subset had low statistical variation and could be represented by the mean. In using this approach, for 0.5% volume additive, there was a 30% increase in lubricity for the ethyl esters over the methyl esters. From the 1.0% additive (Fig. 4), the same trend could be seen, but the result was a 24% increase between the ethyl and methyl esters. The similarity of the percentage increase between ethyl and methyl esters at both 0.5 and 1.0% indicated the same benefit of using ethyl esters over methyl esters, regardless of the percentage of ester added to the sample. This conclusion was supported by a Wilcoxon rank-sum (11,12) test, where for both 0.5 and 1.0% ester addition there was 100% confidence that the ethyl esters performed better than the methyl esters in the HFRR test.

To determine if esters of castor oil were statistically different, the following approach was taken. All data were plotted as shown in Figure 3 for 0.5% volume additive and Figure 4 for 1.0% volume additive to show where the data bars for the

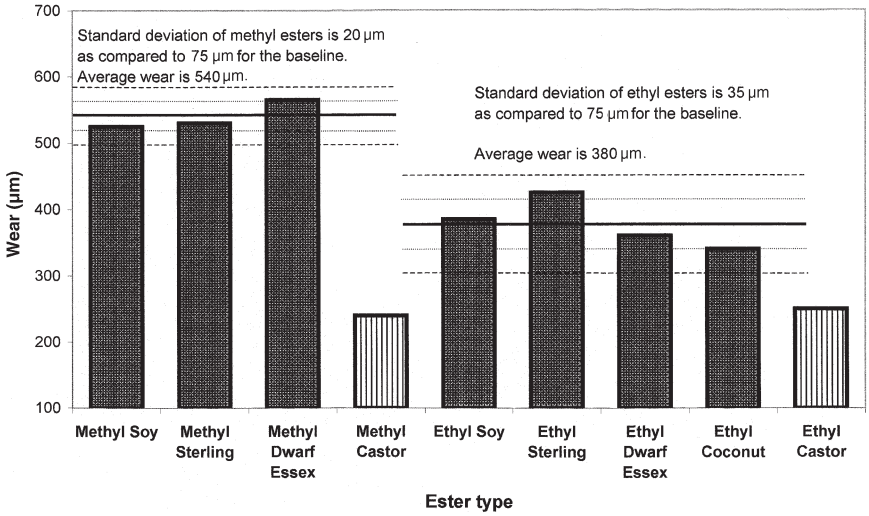

FIG. 3. Wear at 0.5% volume addition of ester. See Figure 2 for explanation of solid, dotted, and dashed horizontal lines. Methyl and ethyl castor esters were evaluated separately from the rest of the esters.

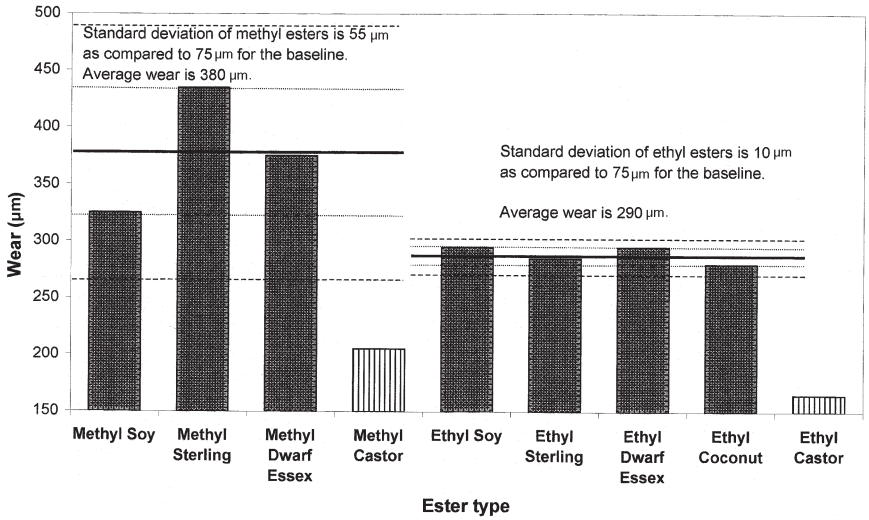

FIG. 4. Wear at 1.0% volume addition of ester. See Figure 2 for explanation of solid, dotted, and dashed horizontal lines. Methyl and ethyl castor esters were evaluated separately from the rest of the esters.

castor oil ester were with respect to the other esters. From Figure 3 one can easily see how the wear for methyl castor lies far below the boundaries of the second standard deviation line, which represents 95% confidence. Again the ethyl castor sample lies outside of two standard deviations for the ethyl esters. The same trend was found for the 1.0% volume additive (Fig. 4). This proves that within 95% confidence the esters of castor oil are statistically different and show improved lubricity over the esters of the other oils tested.

The ethyl esters showed improved lubricity over the methyl esters of the same oil. This research also rejected the hypothesis that the lubricity of the ester was influenced by the length of the carbon chains in the fatty acids of the oil. However, there appeared to be a trend in the kinematic viscosity of the ester with the chain length of the fatty acids in the ester. With the exception of castor, the esters showed increased viscosity for increasingly longer carbon chains. The ester from coconut oil had the shortest carbon chains, as well as the lowest kinematic viscosity. This trend continued up to the longest carbon chains in the Dwarf Essex HEAR.

The conclusion that castor esters have improved lubricity over the other esters was not fully understood. There was a difference in the fatty acid chemical structure, but the free glycerine content and kinematic viscosity measurements were also significantly different. Whether the improved lubricity of castor esters was due to the glycerine retained in the sample or to the attached OH group on the seventh carbon is unknown.

It is important to determine what volume percentage of an ester would be required to meet specific wear limits. The mean data were empirically fit to second-order polynomial

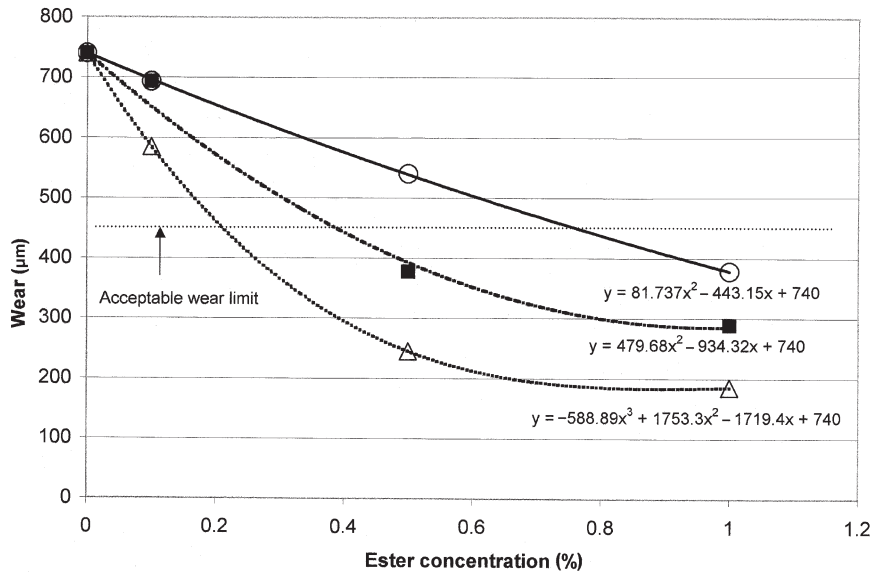

FIG. 5. Wear as a function of ester concentration. ○, All of the methyl esters, taken together; ■, all of the ethyl esters, taken together; △, all of the castor esters, taken together.

equations to produce the plot shown in Figure 5. The *y* in each equation represents wear (μm) and *x* represents the ester concentration (%). To achieve the acceptable maximum wear scar of 450 μm for the U.S. Army specification, about 0.21% of castor ester, 0.39% ethyl ester, and 0.76% methyl ester must be added to the JP-8 fuel. This figure can be used to determine the economic balance between the type of alcohol ester used and the costs to produce enough ester to achieve the desired lubricity enhancement of the ester.

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