BIODIESEL FUELS: THE USE OF SOY OIL AS A BLENDING STOCK FOR MIDDLE DISTILLATE PETROLEUM FUELS

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The U.S. Navy is a very large consumer of middle distillate fuels. Fuels for military applications have more severe restrictions than for the usual commercial consumer. One of the most stringent and difficult requirements to meet is that of fuel storage stability. Storage instability is defined in terms of solids formation which can plug nozzles and filters. Middle distillate fuels for the military can remain unused in storage typically for a year and often much longer. Many fuels show significant deterioration in storage. Storage stability complicates the addition of any other type of natural occurring blending stock. Materials added as fuel blending stocks must be chemically stable and not induce instability in the fuel to which it is added. Furthermore, the blending stock must not react with MILSpec required fuel additives. In the present research, a soybean derived fuel was added in concentrations up to 20% in both stable and unstable petroleum middle distillate fuels. The storage stability of the mixture was tested by ASTM 5304. The soy-fuel mixtures proved stable in the stable fuel and reduced the instability in the unstable fuel significantly.

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ABSTRACT

The U.S. Navy is a very large consumer of middle distillate fuels. Fuels for military applications have more severe restrictions than for the usual commercial consumer. One of the most stringent and difficult requirements to meet is that of fuel storage stability. Storage instability is defined in terms of solids formation which can plug nozzles and filters. Middle distillate fuels for the military can remain unused in storage typically for a year and often much longer. Many fuels show significant deterioration in storage. Storage stability complicates the addition of any other type of natural occurring blending stock. Materials added as fuel blending stocks must be chemically stable and not induce instability in the fuel to which it is added. Furthermore, the blending stock must not react with MILSpec required fuel additives. In the present research, a soybean derived fuel was added in concentrations up to 20% in both stable and unstable petroleum middle distillate fuels. The storage stability of the mixture was tested by ASTM 5304. The soy-fuel mixtures proved stable in the stable fuel and reduced the instability in the unstable fuel significantly.

Key words: middle distillate fuel, biodiesel, soygold, fuel blends

INTRODUCTION

The amount of petroleum fuels produced in the United States continues to decline as both the civilian and military consumption of fuels continues to increase. Many schemes have been proposed to produce middle distillate fuels from sources as diverse as plastic residues, trash, used automobile tires, and from plants - loosely termed biodiesel. The quantities of fuels needed by both the military and other commercial consumers make these schemes daunting in both cost and complexity. If a non-petroleum derived fuel can not be produced with present technology in the quantities required, can a fuel blending stock be produced in significant quantities? As a further complication, military fuels can be stored for periods up to several years before use, but for most typical consumer uses, middle distillate fuels are used almost in the same time frame in which they are produced.

The addition of any material to a petroleum middle distillate fuel must be done with considerable caution for several reasons, among these are: solubility in the fuel at both ambient as well as low temperatures, winter operations in cold climates), flash point considerations, the type of engine in which the fuel will be burned, and preferably less toxic than the fuel itself. However, most importantly the added blending stock must not induce chemical instability in the fuel. Fuel instability problems can be of two related types, short term oxidative instability and long term storage instability.

 The most significant and undesirable instability change in fuel liquids with time is the formation of solids, also termed filterable sediments. These solids can plug nozzles, filters, coat heat exchanger surfaces, and otherwise degrade engine performance. Storage instability has proven to be an intractable problem. A review on fuel instability of about 35 years ago began "The general area of fuel instability is complex and may be considered a black art because not all of the reactions that contribute to instability are known" (1). This statement remains true today. The reactions involved

are still not well understood and further complicates the addition of fuel blending stocks.

Although slight thermal degradation occurs in nonoxidizing atmospheres, the presence of dissolved oxygen or active oxygen species, i.e., hydroperoxides, will greatly accelerate oxidative degradation of fuels as well as significantly lower the temperature at which undesirable product formation occurs. Instability is consequently dependent on the nature of potential autoxidation pathways(2). This further complicates the use of fuel blending stocks.

The rates of reactions in autoxidation schemes are dependent on hydrocarbon structure, heteroatom concentration, heteroatom speciation, oxygen concentration, and temperature (3, 4). Catalysts and free radical inhibitors can materially alter both the rate of oxidation and the reaction pathways (5). Heteroatoms, oxygen, nitrogen, sulfur, and ash have been found to comprise up to 40 percent of deposits that form on hot surfaces (6) such as fuel injectors. The sulfur content of these deposits has been found to vary from 0.3 to 9 percent (7). Sulfur (0.4% military and 0.3% commercial) is the most abundant heteroatom present in middle distillate fuel. The synergism between the various fuel components and hydroperoxides on the stability of middle distillate fuels is not well understood. Differences in fuel composition, reaction surface, quantity of dissolved oxygen, hydroperoxide concentration, and reaction temperature all contribute to the reported variations in fuel deterioration in the literature (8, 9).

In the present research, we report the addition of a soybean derived oil, SoyGold®, in concentrations up to 20% to both stable and unstable middle distillate fuels. The soy-derived fuel makes an excellent blending stock because this particular soy-derived fuel has no organo-nitrogen and organo-sulfur compounds and thus should not enhance or be a participant in the degradation process. This aspect of the research was demonstrated by adding the soy-derived fuel liquids to both a stable

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and unstable petroleum-derived fuel. This material was added in concentration ranges from 10 to 20 volume percent to both a stable and unstable petroleum middle distillate fuel. These fuels have been used in our laboratory for a considerable number of experiments so they are well categorized in their chemical behavior.

EXPERIMENTAL

Instrumental Methods

Gas chromatography.   The samples were analyzed by a Hewlett Packard Model 6890 Gas Chromatograph and data system. An all glass gc inlet system was used in conjunction with a 0.32 mm x 30 m fused silica capillary column, HP cross linked 5% phenyl methyl silicone. The injector temperature was 250°C and the detector was 320°C. The column flow was 1 mL/min. The temperature program started with an initial temperature of 60°C for 5 min, a ramp of 5°C/min, to a final temperature of 260°C. The chromatograms were recorded and integrated on a Hewlett-Packard data system.

Mass Spectrometry.   The soy additive and the soy-fuel mixtures were analyzed by combined capillary column gas chromatography/mass spectrometry, gc/ms. The gc/ms system consisted of a Hewlett-Packard 6890A gas chromatograph configured for splitless injection (1 µL), and a Finnegan INCOS 50B mass spectrometer. The mass spectrometer was operated in the electron impact ionization mode (70 eV) with continuous scan acquisition from 50 to 350 amu at a cycling rate of approximately 1 scan/sec. The parameters were set up with the electron multiplier at 1050 V, source temperature of 200°C, and transfer line temperatures at 290°C. The mass spectrometer was calibrated with perfluorotributylamine prior to use. These gc/ms parameters provided excellent

separation of the compounds in the soy-derived fuel. The INCOS 50 data system and ITDS software were used to process mass spectral information.

Simulated Burner.   A simulated burner was constructed to test nozzle plugging and soot formation from the soy-fuel mixtures. The brass burner consisted of an 1/8" id nozzle orifice surrounded by a ½ air mixing chamber. The outer chamber was drilled and tapped for an 1/8" air line. The fuel was pumped through a 1/4" tube to the nozzle orifice by two syringe pumps, each with a 50 mL capacity syringe. The air was operated at 5 psig or less. The burn of the soy-fuel mixtures were for a period of 15-30 min at which time the burn was suspended and the nozzle examined for deposit formation. A qualitative procedure for measuring soot was also used. It consisted of an inverted 10.5 cm Büchner funnel connected to a vacuum system. After the vacuum was started, a filter was placed in the funnel. The burner was suspended one foot below the funnel and ignited. The filter collected the soot that was formed. The filter was then be weighed to give a measure of the soot formed.

Nuclear Magnetic Resonance. ^{1}H and ^{13}C NMR spectra were acquired in CDCl$_3$ at 300 and 75.0 MHZ, respectively, on a Bruker 300 MHZ spectrometer. ^{1}H chemical shifts are reported in units of ppm downfield from TMS (set at 0.0 ppm). ^{13}C chemical shifts are listed in δ (ppm) relative to chloroform (set at 77.0). Coupling constants, J, are reported in units of Hertz (Hz).

Storage Stability Tests.   The soy-fuel mixtures were tested for fuel instability and incompatibility reactions. They were tested by a modified ASTM method D5304-99 (10). In brief this method is described as: 100 mL samples contained in 125 mL borosilicate glass brown bottles subjected to a 16 hours, 90°C time-temperature regimen at 100 psig overpressure of pure oxygen. After the stress period, the samples were cooled to room temperature. These samples were tested for fuel sedimentation by a gravimetric technique .

Reagents

Soy Diesel Fuel   The soy-derived diesel fuel, SoyGold®, was   supplied by Ag Environmental

Products, 9804 Pflumm Road, Lenexa, KS 66215. This material was light yellow in color, had a

boiling point greater than 400°F, negligible water solubility, a specific gravity of 0.88, and a flash

point of 425°F.

Middle Distillate Fuels The petroleum middle distillate fuels used were from our inventory of tested

fuels. The stable fuel (No. 2 diesel) was an American refined fuel that has been used as a stable fuel

for comparison in our laboratory. This fuel yields 0.6 mg of solids/100mL fuel when tested by the

ASTM D5304 method, and therefore this is classed as a very stable fuel (10). The unstable fuel (our

number NRL 00-3) was a Spanish refined fuel that historically has been unstable, 2.5 mg/100mL or

more of solids formed in the storage stability test procedure. This yield of total solids ranks this fuel

as very unstable.

RESULTS AND DISCUSSION

Diesel fuel is a liquid product distilling over the range 150-400°C (300-750°F). The carbon number

ranges, on average, from about C_{13} to about C_{21}. The chemical composition of a typical diesel fuel

and how it applies to the individual specifications,°API gravity, distillation range, freezing point, and

flash point are directly attributable to both carbon number and compound classes present in the

finished fuel as given in Tables 1 by ASTM D396-96 and ASTM D975-96 (11, 12).

The soy derived diesel fuel offers several attractive advantages for use as a fuel blending

stock. These are summarized in Table 2. The military has many required specifications among these

are those for color, water solubility, flash pont, specific gravity just to mention a few. A comparison

of Table 1 with Table 2 showed that this soy derived bio-fuel would not diminish the quality of a petroleum fuel to which it was added.

The color test, ASTM D-1500, is a color comparison test (13). Consumers buying in bulk generally prefer a lighter colored product. As a fuel degrades, it generally darkens in color. The soy derived fuel and the petroleum-soy mixtures were both observed to be color stable under both low temperature as well as thermal oxidative conditions. It is important to note that a change in color may or may not be related to degradation. However, our laboratory has observed that a color change to dark brown, can be directly correlated with an increasing hydroperoxide concentration and its subsequent reaction with both organo-sulfur and organo-nitrogen compounds (14). The soy-derived diesel does not darken with time even at temperatures of 70°C and exposure to light for a one month time period. These observations are a direct correlation to the chemical components present in the soy blending stock. Analysis showed that the soy blending stock was a mixture of methyl esters of long chain carboxylic acids as illustrated in Table 3. Approximately 75% of the total concentration of the methyl esters consisted of unsaturated compounds as determined by NMR integration. The single peak in the alkoxy region of the ^{1}H NMR spectra, with no sign of splitting indicated the presence of only methoxy esters with no visible sign of carboxylic acid. The identity of the unsaturated alkyl chain was further supported by the integration of the NMR spectra within the olefin region.

^{1}H NMR: δ 5.403-5.323 (m, 3H), 3.663 (s, 3H), 2.772 (t, J = 5.4, 1.5H), 2.302 (t, J = 7.2, 2H), 2.039 (t, J = 6.6, 3.5H), 1.645-1.599 (m, 2.5H), 1.312-1.257 (m, 18H), 0.913-0.869 (m, 3H). ^{13}C NMR: δ 23.16, 24.32, 25.60, 27.16, 29.06, 29.09, 29.12, 29.23, 29.31, 29.49, 29.55, 29.65, 31.50, 34.05, 51.31, 51.34, 127.09, 127.70, 127.88, 128.02, 128.21, 128.24, 129.69, 129.95, 129.97,

130.14, 130.20, 131.89, 174.17, 174.21.

No evidence of organo-sulfur or organo-nitrogen compounds were detected by gc/ms in the soy fuel. Alkyl esters of long chain fatty acids are also thermally stable. This was a further contributing factor to the observed stability of this blending stock and to enhance the storage stability results of the two petroleum derived fuels to which it was added. Likewise, identity of the fuel was further supported by the FT-IR spectra: 3010, 2927, 2855, 1714, 1462, 1436, 1364, 1246, 1197, and 1171 cm^{-1}. which indicated the absence of any $\alpha-\beta$ unsaturated esters. No sign of other functionalities such as carboxylic acid or alcohols were visible in the soyfuel mixture.

The storage stability results are given in Table 4. This ASTM procedure features quite severe reaction conditions. The conditions were: 100mL fuel at 90°C, for 16 hours, at 100 psig pure oxygen. A fuel that survives these drastic conditions should prove stable for more than two years in storage. The results in Table 4 illustrate conclusively that all the soy petroleum middle distillate blends were stable. This was not a total surprise since the soy-derived fuel, Table 3, was composed of methyl esters of long chain fatty acids which are chemical and thermally stable. Esters do not readily form hydroperoxide species and with out a significant concentration of these active oxygen species, a fuel is stable. The lack of peroxidation reactions under the forcing conditions employed illustrated that at ambient conditions the peroxidation reaction could be neglected.

The stability of this blending stock enhanced the observed stability of both the stable and unstable fuel employed as illustrated in Table 4. The unstable petroleum derived diesel has consistently failed the ASTM 5304 storage test procedure (2.5 mg solids/100mL fuel) but, when blended with the soy derived diesel in a 20% matrix, the fuel easily passes the stability test matrix. There are at least two possible explanations for this. In the case of the 20% mixture, the fuel

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concentration is lowered significantly but, most important is that the soy-derived fuel is so stable. The decrease is striking from 2.5 mg of solids to 0.5 mg. The 0.5 mg of total solids is indicative of some of the most stable fuels that we have examined.

For the stable American refined petroleum diesel fuel an improvement was also noted. The petroleum diesel fuel yielded 0.6 mg of solids while the blends gave 0.3 mg for the 10% blend and 0.2 mg for the 20% blend. Again, it was speculated that the noted improvement was a result of the addition of the very stable soy-derived fuel.

The simulated burner experiments were used to check for both deposits that form at the burner nozzle and for soot deposits that result from the flame. The highest concentration of blending stock (20%) was used for these tests. The nozzle was examined after a 30 min burn and nodeposits were observed. Prior experience with this burner indicates that if no deposits are observed at the burner nozzle within 30 min, the fuel can burn almost continuously deposit free (15). The filter paper that was used to monitor soot formation likewise showed no soot deposit by gravimetry. It is important to note that this procedure is for deposit formation due to high temperature oxidative conditions and is not necessarily related to storage instability reactions.

The fuel blends were subjected to one other critical ASTM procedure, that of filterability ASTM D6426 (16). The pure soy-derived fuel would not pass this test but, the 10% and 20% blends passed with ease. Filterability is generally considered to be a measure of fuel cleanliness. However, in the case of the polar esters, it is more probable that there was a chemical interaction with the polar filter media and that the significance of the failure of the neat soy-derived fuel is insignificant. A biofuel that consists mainly of the ester functional group has another major benefit. Fatty acid esters are known to be lubricity enhancers. The addition of 10-20% of this fuel as a blending stock would

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enhance the lubricity of the fuel many fold making fuel pumps and other fuel handling components last longer and thus decreasing consumer operating cost. Finally, this blending stock would also be an internal source of added oxygen to the petroleum derived fuel

CONCLUSIONS

The use of a biodiesel fuel such as Soygold® as a blending stock for middle distillate fuels has many positive attributes. The blending stock meets or exceeds ASTM requirements and definitely showed a positive synergism when mixed with both stable and unstable middle distillate fuels. Blends in the 10% - 20% concentration range yield fuels that are stable in storage for at least a year. Furthermore, these blends also pass the ASTM filterability test. It is worth noting that the pure soy-derived diesel does not pass this test method; however, polar species are known to clog this type of filter. Finally, esters are lubricity enhancers and consequently would have a positive synergism with fuel system components and serve as an additional oxygen source.

ACKNOWLEDGMENT

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TABLE CAPTIONS

TABLE 1
General ASTM Specifications for the Various Types of Diesel Fuels.

TABLE 2
ASTM Methods for Determining Fuel Properties

TABLE 3
Methyl Ester Concentration of Soy-Derived Fuel

TABLE 4
Storage Stability of Soy-Derived and Petroleum-Derived Middle Distillate Fuels

TABLE 1

Specification	Military[1]	No.1-D[2]	No.2-D[3]	No.1[4]	No.2[5]
°API Gravity	44.0	34.4	40.1	35	30
Total sulfur %	0.5	0.5	0.5	0.5	0.5
Boiling point °C	357	288	338	288	338
Flash point °C	60	38	52	38	38
Pour point °C	-6	-18	-6	-18	-6
Hydrogen (wt%)	12.5	- - -	- - -	- - -	- - -
Cetane Number	43	40	40	- - -	- - -
Acid number	0.3	0.3	0.3	- - -	- - -

[1] MIL-F-16884J
[2] High speed, high load engines
[3] Low speed, high load engines
[4] Special purpose burners
[5] General purpose heating fuel oil

TABLE 2

Specification	ASTM Method	Soy-derived diesel Fuel
°API Gravity	D 1298	44
Total Sulfur %	D 129	0
Boiling Point °C	D 86	>400°F (204°C)
Flash Point °C	D 93	452°F (218°C)
Hydrogen (wt%)	D 3701	12.3%
Cetane number	D 613, D 976	not determined
Acid number	D 974	0
Color test	D-1500	passes

TABLE 3

Methyl Ester	Carbon Number	Unsaturation	*Concentration (wt%)
methyl linoleate	C_{18}	2 double bonds	53
methyl oleate	C_{18}	1 double bond	24
methyl linolenic	C_{18}	3 double bonds	3
methyl stearate	C_{18}	saturated	10
methyl palmitate	C_{16}	saturated	10

* trace of other unidentified methyl esters

TABLE 4

Fuels	Solids by Gravimetric Methods In mg/100mL Fuel
Stable Petroleum Diesel	0.6
Unstable Petroleum Diesel	2.5
Fuel Blends	
10% Soy - 90% Stable Diesel	0.3
20% Soy - 80% Stable Diesel	0.2
20% Soy - 80% Unstable Diesel	0.5