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Incompatibility of Recycled Soy-Derived Biodiesels in Marine Environments

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It has been suggested that renewable energy sources be considered as replacements or blending stocks for middle-distillate ground transportation and marine fuels. It is vital for the operational considerations of these fuels to investigate the many positives and negatives that this use could prompt. Unlike air environments, water environments also have a pH factor that has to be considered. Most U.S. Navy shipboard fuel tanks compensate for diminishing fuel by the addition of seawater to the fuel tank. It was found that this practice would lead to fuel instability problems such as filter plugging and potentially other serious engine damage

Introduction

The addition of soybean-derived liquids has been shown to be very functional for middle-distillate ground-vehicle fuels.[1−3] This biodiesel has many similar properties to traditional diesel fuels.[4,5] These properties include similar cetane number, boiling point, distillation range, and carbon numbers but a higher freezing point. Our laboratory has reported that unstable middle-distillate fuels, when 10−20% soy methyl esters were added, unexpectedly became stable fuels and remained so for extended periods of time, a year or more.[3] These same soy-derived esters also behave in a similar fashion with unstable jet fuels, but because of freezing point consideration they cannot be used for aircraft fuels.[4]

The military is currently considering allowing 10−20% of these materials to be added to diesel fuels. Our laboratory's experience with these recyclables is mixed. Some remanufactured soy methyl esters have been excellent when added to fuels, while other samples have been poor in that the biodiesel itself was unstable and, even worse, they converted stable fuels to unstable fuels. The soy liquids that have induced instability in fuels were found to have acidic components remaining that were not methylated during the remanufacturing process. In some petroleum diesel fuels, the presence of even a few ppm of carboxylic acids has been shown to induce instability reactions in other stable fuels.[6,7] However, when new or remanufactured soy liquids are added to middle-distillate fuels that are used in marine environments, the situation is drastically changed. In most large military ships, the use of seawater compensating fuel tanks is standard practice. This is the problem that is addressed in this report. We identify the components that react when exposed to seawater.

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Experimental Section

General Methods. Unless otherwise stated, chemicals were reagent grade and were obtained from commercial sources and used without additional purification

Soy-Derived Biodiesel Fuel. The recycled soy-derived biodiesel liquid was supplied by a large eastern United States recycling company. It had a boiling point >400 °F, negligible water solubility, a specific gravity of 0.86, and a flashpoint >300 °F. No information on its cetane number was supplied. However, newly manufactured soy liquids greatly exceed the minimum ASTM required cetane number of 45.[5] No antioxidant was added after reprocessing. This soy liquid was a yellow−brown colored liquid as received. It was stored under refrigeration until used.

Extraction Procedure. Initially, a 150-mL sample of recycled, soy-derived biodiesel was extracted by a fresh 750-mL sample of seawater prepared by ASTM D-1141-52, Formula A. This seawater solution was filtered and had a pH of 8. The ASTM seawater salts were used to avoid the organic contaminants present in actual seawater collected close to shore. The seawater and biodiesel were placed in a clean, 2 L brown borosilicate bottle and stirred with a Teflon stirring bar for 48 h in the dark. The layers were separated with the emulsion layer retained with the soy layer. This was done because the emulsion could not be broken by the usual chemical methods. The water layer was acidified with 1M HCl and then extracted with 500 mL of methylene chloride. A dilute HCl solution was used so that no induced chemical reactions occurred. The methylene chloride was then dried with anhydrous magnesium sulfate and reduced in volume to 10 mL under reduced pressure. The heavy emulsion layer was then separated from the soy liquid, and the soy liquid was dried with molecular sieves before analysis.

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 tetramethylsilane (TMS) (set at 0.0 ppm). [13]C chemical shifts are listed in δ (ppm) relative to chloro-

Table 1. Methyl Ester Concentration in Recycled Soy-Derived Fuel Liquid

methyl ester	carbon number	concentration[a] (wt %)
methyl linoleate	C_{18}	53
methyl oleate	C_{18}	24
methyl stearate	C_{18}	10
methyl palmitate	C_{16}	10
methyl linolenate	C_{18}	3

[a] Traces of other unidentified methyl esters.

Table 2. Acid Components Present in Recycled Soy Cooking Oil.

carboxylic acid	area[a] (%)
malonic	1
hexanoic	8
hex-3-enoic	2
non-3-enoic	3
nonanoic	2
nonanedioic	1
dodec-3-enedioic	1
octadeca-9,12-dienoic	18
octadeca-9-enoic	1

[a] The numbers are expressed as the relative area percent from this extract.

Figure 1. Reaction scheme for recycled soy.

form (set at 77.0). Coupling constants, J, are reported in units of Hertz (Hz).

Mass Spectrometry. The soy liquid extract was analyzed by combined capillary column gas chromatography/mass spectrometry, gc/ms. The gc/ms system consisted of a Hewlett-Packard 5890 Series II gas chromatograph configured for split flow injection (3:1),- and a Hewlett-Packard 5971 series mass selective detector. The gc was equipped with an all-glass inlet system in conjunction with a 0.20 mm × 50 m poly-(dimethylsiloxane) capillary column (HP-1, 19091Z-105) made by Agilent Technologies. The injector temperature was 250 °C, and the detector temperature was 280 °C. The column flow was 1 mL/min. The temperature program started with an initial temperature of 60 °C for 3 min, used a ramp of 3 °C/min, and went to a final temperature of 290 °C that was held for 2 min. A solvent delay of 5 min was also incorporated into the temperature program. The mass spectrometer was operated in the electron impact ionization mode (70 eV) with continuous scan acquisition from 35 to 550 amu at a cycling rate of ~150 scans/s. The parameters were set up with the electron multiplier at 1212 V. These gc/ms parameters provided excellent separation of the compounds in the soy-derived fuel. The HP, MS Chem Station hardware 61701BA version B.01.00 was used to process mass spectral information.

Results and Discussion

It has been suggested that renewable energy sources be considered as replacements or, at least, as a blending stock for middle-distillate fuel applications. This is even truer today with high petroleum prices and seasonal scarcities in the middle-distillate fuel market. However, before any commitment to add or exclusively use biofuels, it is vital for operational considerations to investigate the many positives and negatives that this use could prompt.
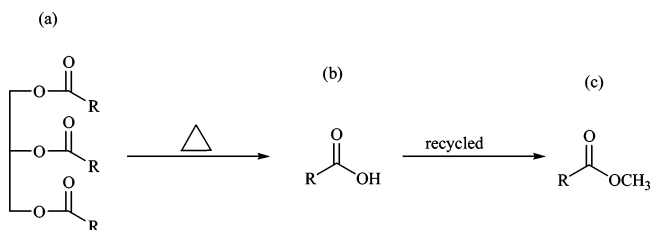
Table 1 illustrates the results from gc/ms analysis of the recycled soy-derived liquid that was investigated. It consisted primarily of C_{16}–C_{18} methyl esters. The concentration of each ester is expressed in terms of weight percent. The recycled soy liquid was a brown color, while the newly manufactured soy liquid was a pale yellow. We have noted that, when a petroleum fuel starts changing color, it can be indicative of chemical reactions that lead to instability changes in the fuel.[7]

For comparison, the gc analysis of newly manufactured soy liquid was performed. It gave a practically identical product slate to that of the recycled soy liquid. In the presence of the major component listed, it was not possible to identify the minor carboxylic acid components present. Consequently, a mild basic extraction of both the newly manufactured and the recycled soy

liquids that are the subject of this report was performed. The total amount of acidic materials detected was ~1% by weight in the recycled soy-derived biofuel, as illustrated in Table 2. It has been reported that only a few parts-per-million of total carboxylic acids will significantly degrade petroleum-derived diesel fuels.[7,8] Thus, in proposing a biofuel replacement or a biofuel blending stock, consideration must be given to these problems that minor components could cause. Relative area percentages were used for these components since the total concentration in weight percent of all acidic components was only ~1%. It is to be noted that, after the seawater extraction procedure, no acidic materials were detected by either combined capillary column gc/ms or NMR (nuclear magnetic resonance). However, the acid material contributed to the large emulsion layer that was noted.

The fact that most large military ships use seawater-compensating fuel tanks for ship stability purposes can magnify the problem that petroleum-only fuels already cause. At the petroleum fuel−water interface in these tanks, problems such as bacterial growth and fuel−water emulsions continue to be a problem with middle-distillate fuels. The problems will be magnified if biodiesels are permitted in marine diesel fuels. Operationally, because of the chemical nature of the soy-derived fuel liquid and the alkaline nature (pH ≈ 8) of seawater, an intractable emulsion layer was formed at the water−fuel interface. This material has a soap-type consistency and could not be broken or reduced by the usual chemical means. We have confirmed that not all of the fatty acids in recycled soy cooking oils were converted to the corresponding methyl ester. This is, in all probability, the chemical source of the soap-type solid.

Figure 1 represents an idealized scheme for the recycling of the soy-derived restaurant cooking oil. However, this scheme cannot explain the compounds listed in Table 2. The acidic components in this table have not been found in newly manufactured soy methylated ester liquids that our laboratory has examined. A more complicated mechanism must be used to explain their formation in recycled soy liquids.
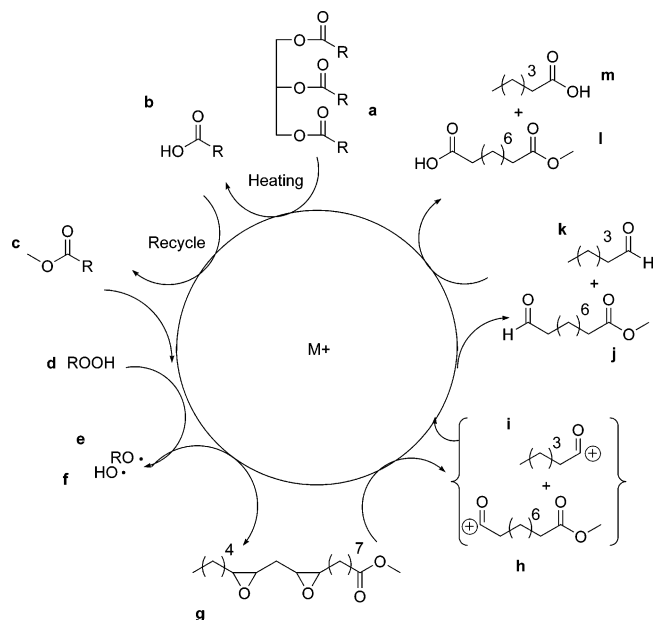
Figure 2. Byproducts resulting from the decomposition of the cooking cycle.

Figure 2 depicts a proposed outline for the formation of the observed carboxylic acids illustrated in Table 2. This figure is meant to be inclusive of all of the compounds that could be formed starting with soy cooking oils on prolonged heating, such as in restaurants applications. Saponification and cleavage reactions of these triglycerides (a) into the corresponding carboxylic acids (b) is well-known.[9,10] Subsequent recycling of these liquids utilizing standard esterification procedures, typically catalytic amounts of acid in the presence of an alcoholic solvent such as methanol, results in the corresponding methyl ester (c). When unsaturated esters such as the esterified product of octadeca-9,12-dienoic acid are present and react with a catalytic amount of radical (e or f), resulting from the decomposition of peroxide (d), they are known to result in the oxidation of the units of unsaturation to afford the corresponding epoxide.[11,12] Although it is known that there exist chances of single epoxidation, for simplicity, the diepoxy (g) is depicted.

Thermal decomposition could easily result in the corresponding carbocations (h and i); however, because they are believed to be either low in concentration or fleeting intermediates, they are not detected in the analysis. This reaction is promoted not only by the presence of metal surfaces such as those present in industrial cooking devices but also by the presence of polar protic solvents such as those used in the recycling procedures. These polar protic molecules would easily result in the immediate formation of the corresponding aldehydes (j and k), which then convert into the more stable oxidized form, the carboxylic acids (l and m). These compounds were detected in notable quantities by gc/ms and are listed in Table 2. Hexanoic acid (m) and decanedioic acid monomethyl ester (l) are the resulting decomposition products of the starting material, octadeca-9,12-dienoic acid, in this reaction cycle.

Acidic compounds found in the recycled soy oil sample probably resulted from both the temperature and the time period for which these restaurant cooking oils were used. Recycling and distillation removed most of the acid components (>99%), but the remaining acids were responsible for the observed fuel deterioration.
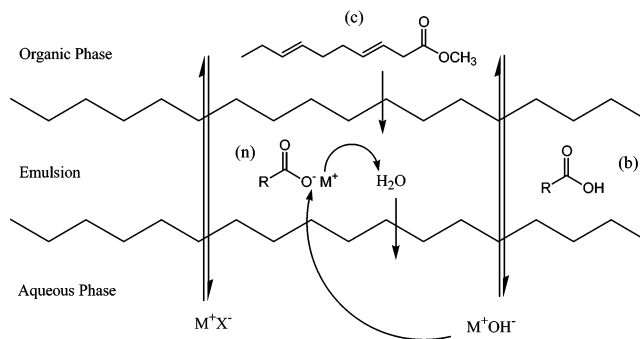

Figure 3. Extraction phase mechanism for recycled soy. Notes: (1) There is no heat involved in the extraction procedure; therefore, no radicals are formed. (2) Because of the aqueous quenching in the extraction, no carbocations should remain.

Figure 3 illustrates the complicated nature of the emulsion that formed. After mixing with the seawater, the acidic components that were in the soy liquid were completely removed (gc/ms). When the emulsion layer was collected and acidified with 6M hydrochloric acid and then this water layer was extracted with methylene chloride, it was possible to detect the acidic components listed in Table 2.

During the extraction procedure, it was obvious that the emulsion region was not simply an interface between two materials of differing density but was a chemically active zone for most of the decomposition of the soy fuel liquid. Because of the unique soy biodiesel/seawater interface, a unique emulsion resulted. This emulsion was compatible not only with the sea salts but also with the larger organic molecules. This layer was also found to extract many of the polar acidic impurities found in the recycled fuel. Moreover, dimerizations of fatty acids are documented to proceed in emulsions, especially when a catalytic amount of oxygen is present to catalyze what is believed to be a Diels−Alder [4 + 2] cycloaddition.[13] In addition, any of the six-member ring adducts, especially those possessing a carboxylic acid functionality over the methyl ester, can then react with any trace amines in the fuel, resulting in amide formation and, consequently, the promotion of a hydrogellike formation within the emulsion layer. In commercial emulsion products such as paints and coatings, this formation is retarded by the addition of a surfactant. The lack of surfactant and the inseparable emulsion layer are additional evidence that this formation is taking place.

Upon comparison of the soy fuel before and after seawater extraction (original, a, and after seawater extraction, b) by ^{1}H NMR, it was determined that both were practically identical in terms of chemical composition, with both consisting of the same slate of methyl esters; see Table 3. However, it was noted that the alkyl functionality was slightly different. There was an ~3% increase in the amount of alkyl functionality observed in b compared to a. Both soy liquids had the same relative amount of methyl ester. There was, however, a 3% decrease in the terminal vinylic character in extract b.

Thus, when soy biodiesel liquids are used either pure or in blends, heavy emulsions are formed when in contact with water. The formation of these intractable emulsion layers would cause great operational difficulties for ships that use water-compensating fuel tanks. Biodiesels must be avoided for marine applications.

Table 3. A. ^{1}H NMR Data for Recycled Soy-Derived Fuel Blending Stocks A and B

functionality	δ	integration	signal	remarks
		a. Original		
$-CO_2CH_3$	3.66	1	S	only methyl ester
$-HC=CH-$	5.43−5.24	1	M	no conjugation
$-CH_3$	0.89	0.94	T	90% alkyl
	0.97	0.11	T	10% vinyl
$-CH_2CO_2R$	2.30	0.69	T	unconjugated
	2.79	0.44	T	$\gamma-\delta$ unsaturation
$-CH_2-$	1.62	0.72	T	alkyl
	1.32−1.23	5.75	M	alkyl
	2.11−1.97	1.13	M	alkyl
		b. After Seawater Extraction		
$-CO_2CH_3$	3.66	1	S	only methyl ester
$-HC=CH-$	5.43−5.24	1	M	no conjugation
$-CH_3$	0.89	0.97	T	93% alkyl
	0.97	0.08	T	7% vinyl
$-CH_2CO_2R$	2.30	0.68	T	unconjugated
	2.79	0.44	T	$\gamma-\delta$ unsaturation
$-CH_2-$	1.62	0.71	T	alkyl
	1.32−1.23	5.73	M	alkyl
	2.11−1.97	1.11	M	alkyl

Conclusion

Biodiesel materials have been found to be an excellent diesel fuel substitute for both civilian as well as military ground-transportation vehicles. However, they cannot be used for marine applications when seawater-compensating fuel tanks are involved. A seawater extraction of a recycled soy-derived liquid was carried out. The separation of the oil−water layers was difficult because of a heavy soapy emulsion at the interface. The soapy emulsion was from the reaction of trace acid materials with the alkaline seawater. It was apparent that current recycling methods used by this manufacturer did not remove acidic components. The use of recycled restaurant cooking oils is a laudable goal, but the recycled material must be further treated so that it does not cause problems to the petroleum fuel to which it is added. As presently constituted, this recycled product could be used only in ground-transportation fuels. Its shipboard use must be discouraged, since the emulsion layer would plug nozzles and filters and damage engine parts with the ingestion of the seawater in the heavy emulsion layer.

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