

Naval Surface Warfare Center Carderock Division

West Bethesda, MD 20817-5700

NSWCCD-61-TR-2008/15 September 2008

Survivability, Structures, and Materials Department
Technical Report

The Explicit and Implicit Qualities of Alternative Fuels: Issues to Consider for Their Use in Marine Diesel Engines.

by

David M. Stamper and Gilbert F. Lee



Approved for public release; distribution is unlimited. September 2008.

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Enclosure (1)

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 30-Sep-2008		2. REPORT TYPE Final		3. DATES COVERED (From - To) 1-Feb-2008 - 30-Sep-2008
4. TITLE AND SUBTITLE The Explicit and Implicit Qualities of Alternative Fuels: Issues to Consider for Their Use in Marine Diesel Engines.			5a. CONTRACT NUMBER N0001408WX20657	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) David M. Stamper and Gilbert F. Lee			5d. PROJECT NUMBER 08-1-6170-501-10	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) Naval Surface Warfare Center Carderock Division 9500 MacArthur Boulevard West Bethesda, MD 20871			8. PERFORMING ORGANIZATION REPORT NUMBER NSWCCD-61-TR-2008/15	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Robert A. Brizzolara Office of Naval Research 875 N. Randolph St. Arlington, VA 22203			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release. Distribution unlimited.				
13. SUPPLEMENTARY NOTES				
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15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 39
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED		
				19a. NAME OF RESPONSIBLE PERSON David Stamper
				19b. TELEPHONE NUMBER (include area code) 301-227-0329

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Administrative Information

This critical analysis and literature review of fuel quality issues was performed at the Naval Surface Warfare Center, Carderock Division (NSWCCD), West Bethesda, MD in the Survivability, Structures and Materials Department by the Non-metallic Materials Research and Engineering Branch (Code 617). This work was funded by the Office of Naval Research.

Executive Summary

This report describes the explicit and implicit properties of petroleum-derived fuels and the alternative Fischer-Tropsch (F-T), pyrolysis, and biodiesel fuels. These alternative fuels are compared to two jet fuels (JP-5 and JP-8) and distillate fuel marine (DFM- marine diesel fuel). The explicit properties of military fuels are found in the military specifications (MILSPECs) of the several fuels. The DFM MILSPEC successfully predicts the suitability of petroleum-derived fuel in the marine diesel engine application. Implicit properties are those characteristics either derivative of the MILSPEC properties or testing methods, or may be unrelated to the MILSPECs, having been found in other literature. The implicit properties of a petroleum-derived fuel do not typically need to be determined or are sufficiently implied by other measurements, given the long history of petroleum use. Fuels derived from sources other than petroleum, however, can be sufficiently different that implicit fuel properties that are not typically measured become important.

Broadly speaking, unfinished or raw F-T and pyrolysis fuels are sufficiently dissimilar to petroleum diesel or jet fuels, such that using them directly would be problematic. However, such unfinished fuels are unlikely to be commercially available. Finishing those fuels by hydrotreating to remove excess oxygen and saturate double bonds, and distillation over the appropriate temperature ranges will produce a fuel very similar to petroleum fuels. Finished F-T and pyrolysis fuels can meet most of the MILSPEC explicit properties, but may have a problem meeting energy density requirements. In comparison, biodiesel does not meet several explicit properties because of higher acidity, viscosity, instability, pour point, and metals and ash content, as well as a lower energy density. Seawater contamination of biodiesel blends is particularly problematic, leading to increased water emulsification, microbial growth, and filter clogging.

Several implicit properties of alternative fuels may be problematic for use in marine diesel engines. Finished F-T fuels are composed primarily of *n*- and *iso*-paraffins, with very low heteroatom, aromatics, and cyclo-paraffins content. This results in a lower density and lower bulk modulus fuel, with implications for fuel delivery and injection timing issues, seal failure, and low lubricity. Biodiesel has a higher oxygen content, leading to higher surface tension, and a high bulk modulus. These affect fuel delivery and injection timing, and combustion kinetics. The high oxygen content is good for lubricity, however. The extent to which these issues actually affect marine diesel engines has yet to be determined in most cases.

Blending alternative fuels with petroleum fuels will mitigate most implicit problems of the alternative fuels. Use of a high-pressure, “common rail” fuel injection system would eliminate the issue of bulk modulus affecting fuel injection timing. Additives would improve the remaining limiting properties of F-T and biodiesel fuels. Lubricity additives should remove the potential liability of the low lubricity of F-T fuel. Antioxidant additives can improve the stability of biodiesel, but the water contamination issues with biodiesel remain problematic.

Introduction

As alternative fuels gain a larger share of the commercial market, it is important to assess their suitability for use by the U.S. Navy. This report examines the implications of using several alternative fuels in existing marine diesel engines and advanced engine designs. The alternative fuels most likely to be encountered by the U.S. Navy are pyrolysis, Fischer-Tropsch (F-T), and biodiesel fuels. This report covers each of these alternative fuels, their varieties, and the processing methods that impact on fuel properties. A focus of this report is to determine the implicit properties of aviation (JP-5/JP-8) and marine diesel fuel (DFM), and how alternative fuels may differ in these implicit properties. Implicit properties are those properties either derivative of the MILSPEC properties and testing methods, or may be unrelated to the MILSPECS, having been found in other sources of information.

MILSPECS have a long history of adequately describing the suitability of petroleum-derived fuels. The concern is that fuels that are derived from sources other than petroleum may be sufficiently different to cause problems, even if they could meet the explicit requirements in the MILSPECS. F-T, pyrolysis, and biodiesel fuels typically contain fewer chemical compounds than petroleum fuels and, as will be described, may lack entire classes of compounds. As an example, biodiesel derived from soybean oil is ~90 percent methyl esters of 18-carbon fatty acids (Haas et al. 2001). Important differences between petroleum and alternative fuels may only be apparent in implicit fuel characteristics and/or properties that are not typically determined.

The fuels described in this report were chosen because they have high energy contents and/or are produced in such quantities that the Navy engines cannot avoid exposure to them. The alcohol fuels are not included in this report because they have a low energy density, a low flash point, and are much less suitable for blending with military fuels like JP-5, JP-8, or DFM. A prime consideration for militarily useful alternative fuels is their energy density. In this regard, F-T and some pyrolysis fuels are preferable since they can be made with an energy density similar to petroleum fuels. In contrast, because of its oxygen content, biodiesel only manages 85-90 percent of the energy density of petroleum fuels, and even a small decrease in performance is detrimental. However, biodiesel is currently being produced in large quantities as a transportation fuel and may be blended with diesel fuel that could make its way into U.S. Navy tactical fuel supplies. For this reason, the full implications of using biodiesel must be investigated and understood along with F-T and pyrolysis fuels.

Petroleum Fuels

Petroleum fuels are a complex mixture of numerous and varied hydrocarbons and other organic compounds. Hydrocarbons are those compounds containing only carbon and hydrogen. Examples of the classes of compounds found in petroleum and petroleum-derived fuel are shown in Figure 1. The most abundant classes of organic compounds in liquid petroleum fuels are the paraffins, cycloalkanes, alkenes, and aromatics. In the petroleum industries, alkanes, cycloalkanes, and alkenes are commonly termed paraffins, naphthenes, and olefins, respectively. Minor constituents of petroleum include organic compounds containing the heteroatoms (other than hydrogen or carbon) nitrogen, sulfur, and/or oxygen.

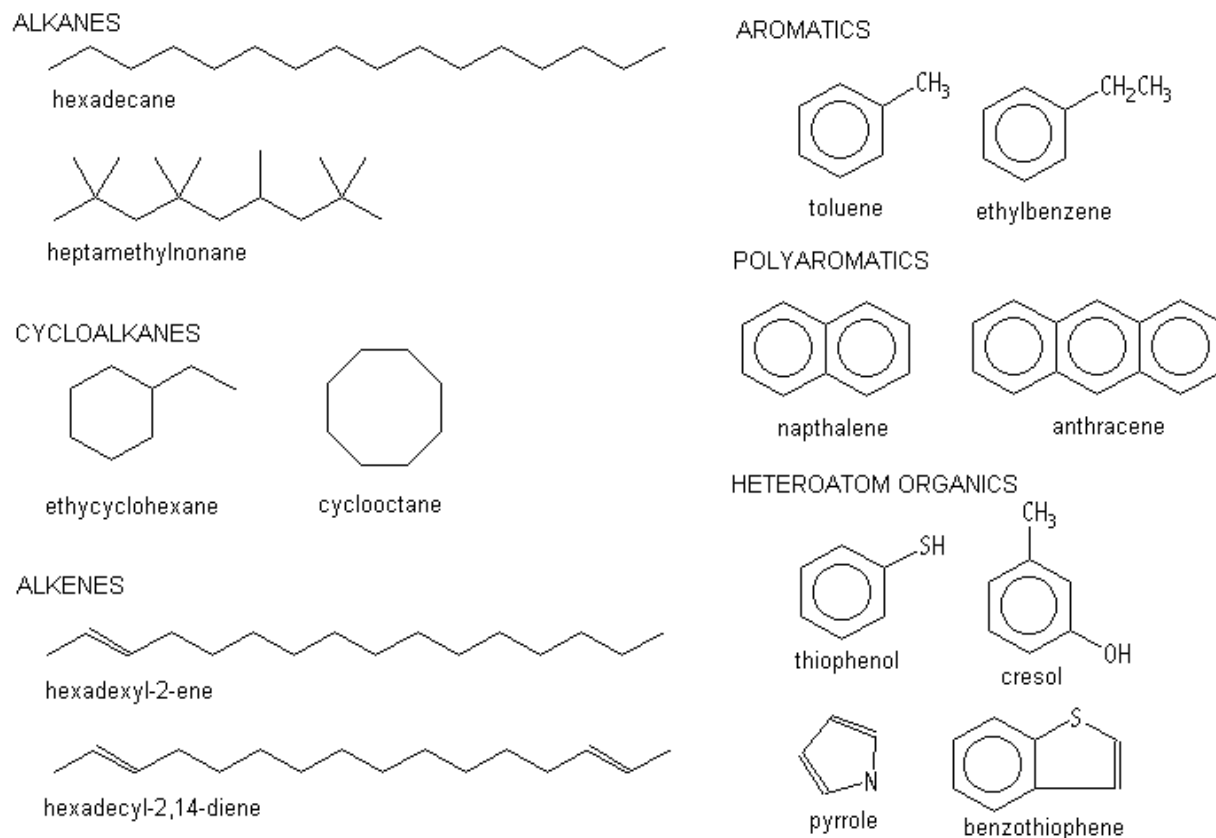


Figure 1. Examples of organic compounds in petroleum.

Fuel compositions are variable, depending on the petroleum stock and the refining processes that are applied. Petroleum stocks vary in density, viscosity, and other bulk properties that reflect their chemical composition, with certain stocks being better suited for certain products. The refining process is modified to accommodate different petroleum stocks. The long history of liquid fuels derived from petroleum has established the correlations between the measured fuel properties and performance. Consistent with this long experience, the military specifications (MILSPECs) for aircraft turbine fuel and diesel fuel have, until recently, insisted that such fuels be derived from petroleum sources.

Properties like viscosity, density, and distillation range are affected primarily by the bulk chemical composition. For *n*-alkanes (paraffins), longer chain molecules have higher boiling points, density (Table 1), and viscosity (not shown). Density levels off around a length of about 20 carbons, however. Beyond this general relationship between molecular weight and bulk properties, the relative amounts of cycloalkanes (naphthenes), branched alkanes (*iso*-paraffins), and aromatics also play an important role. As demonstrated in Table 1, naphthenes and aromatics are denser and have higher boiling points than their corresponding paraffin. Because of increased polarity and/or hydrogen bonding (Cary 1987), substitution of a carbon with an oxygen or a nitrogen dramatically increases the density, boiling point, and viscosity. As will be described in the discussion of diesel fuel, a higher boiling range and lower density provide a higher cetane index. Thus, an abundance of *iso*-paraffins such as 2,2-dimethylbutane (Table 1), tend to decrease the cetane index of a fuel.

Table 1. Selected properties of several petroleum constituents.
Relative boiling point and density are compared to *n*-hexane (Weast et al. 1984).

Chemical Compound	Mol. Formula	Mol. Weight	Boiling Pt. (°C)	Relative Boiling Pt.	Density (g/mL)	Relative Density	Comments
Comparison of <i>n</i>-Alkanes in the Liquid to Solid Range							
Pentane	C ₅ H ₁₂	72.2	36	58 %	0.626	94.8 %	Lightest, most volatile
Hexane	C ₆ H ₁₄	86.2	69	100 %	0.660	100 %	Basis for comparison
Heptane	C ₇ H ₁₆	100.2	98	142 %	0.684	103.5 %	
Octane	C ₈ H ₁₈	114.2	126	183 %	0.703	106.4 %	
Nonane	C ₉ H ₂₀	128.3	151	219 %	0.718	108.7 %	
Decane	C ₁₀ H ₂₂	142.3	174	252 %	0.730	110.6 %	
Dodecane	C ₁₂ H ₂₆	170.3	216	313 %	0.749	113.4 %	
Hexadecane	C ₁₆ H ₃₄	226.5	287	416 %	0.773	117.1 %	18.2°C melting point
Eicosane	C ₂₀ H ₄₂	282.6	343	497 %	0.789	119.4 %	Solid, density levels off
Hexacosane	C ₂₆ H ₅₄	366.7	412	597 %	0.778	117.9 %	Beyond diesel distillation endpoint
Comparison of Several Similar Molecular Weight 5- and 6-Carbon Liquid Compounds							
Hexane	C ₆ H ₁₄	86.2	69	100 %	0.660	100 %	Basis for comparison
1-Hexene	C ₆ H ₁₂	84.2	63	91 %	0.673	101.9 %	Unsaturated
2,2-Dimethylbutane	C ₆ H ₁₄	86.2	50	72 %	0.791	119.8 %	Isomer
Cyclohexane	C ₆ H ₁₂	84.2	81	117 %	0.779	117.9 %	Cyclic isomer
Cyclohexene	C ₆ H ₁₀	82.2	83	120 %	0.810	122.7 %	Cyclic unsaturated
Methylcyclopentane	C ₆ H ₁₂	84.2	72	104 %	0.749	113.4 %	Cyclic isomer
Ethylcyclobutane	C ₆ H ₁₂	84.2	71	103 %	0.728	110.3 %	Cyclic isomer
Benzene	C ₆ H ₆	78.1	80	116 %	0.877	132.7 %	Aromatic w/ 6 carbons
Pyridine	C ₅ H ₅ N	79.1	115	167 %	0.982	148.7 %	Heterocyclic aromatic
Cyclopentanone	C ₅ H ₈ O	84.1	131	190 %	0.949	143.7 %	Cyclic w/ keto-oxygen
Cyclopentanol	C ₅ H ₉ OH	86.1	141	204 %	0.948	143.5 %	Cyclic w/ hydroxyl

Crude petroleum is composed of a wide range of gaseous, liquid, and solid compounds dissolved together. Crude petroleum is not directly suitable as fuel for most uses, and must be processed into the various fuels with which we are familiar. The major liquid fuels produced from petroleum are gasoline, kerosene, and diesel, which differ in the ranges of molecular weights and types of constituent organic compounds. Gasoline contains mainly compounds with 5-12 carbons, with an abundance of aromatic compounds. The military jet fuels JP-5 and JP-8 are derived from kerosene, which consists primarily of paraffin and naphthene compounds with 7-16 carbons. Diesel fuel is similar to kerosene, but is heavier, with 10-22 carbons and frequently has a higher aromatic content.

Various processes are performed in an oil refinery, depending on the available feedstocks and the demands for particular fuels. Among the various processes, distillation is universal, separating petroleum constituents based on their boiling ranges into various gaseous, liquid, and solid (wax, asphalt, and coke) fractions. Liquid fractions are often separated into naphtha (gasoline), kerosene, and diesel fraction, from lowest to higher boiling ranges. Gasoline production typically depends on several processes, including distillation, cracking, and reforming. After distillation, heavy residues are typically cracked by heating over catalysts to fragment the larger paraffins into shorter paraffins and olefins, which are reformed into aromatic compounds

for high-octane gasoline. If it were not for cracking and reforming, the yield of gasoline from crude petroleum would be inadequate for contemporary needs. Kerosene and diesel are often simple distillate fuels, fractionated from crude petroleum by their boiling ranges, although cracked stocks may also be used.

Hydrotreating is another important refinery process, performed primarily to eliminate nitrogen, oxygen, and/or sulfur compounds. Hydrotreating may also be performed to saturate olefins in order to improve fuel stability. Hydrogen (H_2) is added at high pressure and temperature, in the presence of catalysts, to reductively hydrogenate various compounds (Figure 2). The amounts of sulfurous and nitrogenous compounds in fuel are regulated because when they are burned, they produce sulfur dioxide (SO_2) and nitrogen oxides (NO_x) that combine with water to form acid rain. Sulfur also contaminates and deactivates certain catalysts used in petroleum refining. Oxygen compounds are typically less abundant in petroleum, but are important for fuel lubricity (Hughes et al. 2002, 2003).

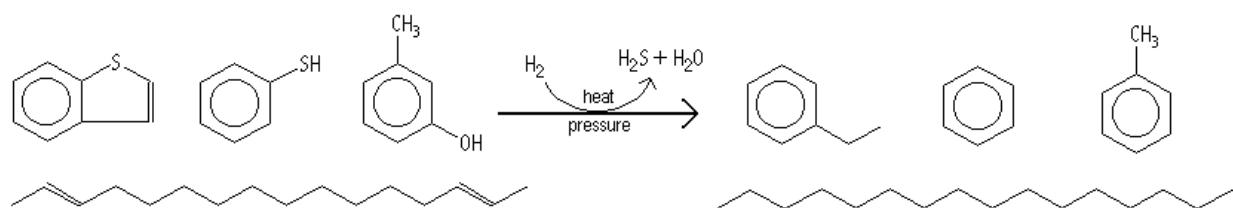


Figure 2. Hydrotreating sulfur- and oxygen-containing compounds and olefins. Although not shown, hydrotreating can also saturate and cleave aromatic rings.

The U.S. Navy relies largely on two different liquid fuels for tactical purposes. The first is distillate (or diesel) fuel marine (DFM), also called F-76. JP-5 is the second main fuel. This is a kerosene based, lower-boiling range fraction than diesel, with specifications for a significantly higher flash point ($60^{\circ}C$) than the jet fuel used by the U.S. Air Force, JP-8. This is done for safety reasons, as JP-5 is both harder to ignite and fires spread more slowly than those from JP-8 (Wells et al. 1998).

Both turbine and diesel engines are flexible with regard to the fuels they burn and can typically run successfully on either kerosene or diesel fuel. There are issues with running diesel engines on kerosene fuel, as well as running turbine engines on diesel fuel, however. Running diesel engines on kerosene can be problematic because kerosene tends to have lower lubricity. Low lubricity, also a problem with some synthetic fuels, adversely affects fuel pumps and injectors (Stavinoha et al. 2004; Frame and Alvarez 2003). The issue of fuel lubricity is further addressed below in discussing diesel fuel.

Because there is more flexibility in the fueling of diesel engines and less flexibility with regard to aircraft turbine engines, the overall Department of Defense (DoD) strategy is to have a single, kerosene-based battlefield fuel (the single fuel concept, SFC). Sea-based forces are moving in the direction of using JP-5 as the main fuel, while land-based forces consider JP-8 as the main battlefield fuel. The SFC eliminates the possibility of mis-fueling and simplifies the logistical chain (Le Pera 2005; Giannini et al. 2002; Sermarini 2000). Alternative fuels are compliant with the SFC to the extent that they meet the JP-5/8 MILSPECS, with the caveats described below for the implicit properties.

Military Jet Fuels: JP-5 and JP-8

Jet fuels originate with the kerosene fraction of petroleum, and are composed of hydrocarbons with 7-16 carbons. JP-5 and JP-8 are very similar in most respects, with the main difference being that JP-5 specifies a flash point of $\geq 60^{\circ}\text{C}$ (Table 2). The higher flash point means that less of the more volatile kerosene compounds will be found in JP-5. The newest JP-8 MILSPEC (MIL-DTL-83133F, April 2008) permits blending up to 50 percent (finished) F-T fuel with petroleum JP-8.

Table 2. Differences between MIL-DTL-5624U (JP-5) and MIL-DTL-83133F (JP-8) requirements.

Fuel Property	JP-5 Value	JP-8 Value	Comments
Flash Point	$\geq 60^{\circ}\text{C}$	$\geq 38^{\circ}\text{C}$	JP-5 has much higher flash point requirement
Freezing Point	$\leq -46^{\circ}\text{C}$	$\leq -47^{\circ}\text{C}$	Very similar
Density (g/mL) @ 15°C	0.788-0.845	0.775-0.840	Very similar
Heat of combustion, MJ/kg	≥ 42.6	≥ 42.8	JP-8 slightly higher
Water separation interface rating	--	1b	No spec for JP-5
Fuel electrical conductivity	--	150-450 pS/m	No spec for JP-5
Naphthalene, vol	--	$\leq 3\%$	No spec for JP-5
Source	Petroleum Only	$\leq 50\%$ synthetic	Synthetic Paraffinic Kerosene (F-T fuel) meeting specifications of Appendix A in JP-8 MILSPEC.

In addition to the appropriate kerosene fraction, JP-5 contains 17.2-24.0 mg/L of various tert-butyl phenols as antioxidants. JP-5 may also contain the metal deactivator (chelator) 2.0-5.7 mg/L N,N'-disalicylidene-1,2-propanediamine. These additives serve to increase the storage stability of JP-5 by limiting the formation of peroxides and free radicals. Corrosion inhibitors, lubricity improvers, and fuel system icing inhibitors are also added, according to the provisions of the MILSPEC for JP-5 (MIL-DTL-5624U). Table 3 briefly describes the several American Society for Testing Materials (ASTM) methods used to analyze the fuel and the values required to meet the JP-5 MILSPEC. Table 3 also contains brief descriptions of the implicit and/or explicit properties of those ASTM methodologies and MILSPEC requirements. These properties are discussed below.

Implicit and/or Explicit Properties of JP-5

JP-5 has 19 properties that must be separately determined and two standard practices that must be followed while measuring those properties. Some properties can be determined using any of two or more methods. For example, seven ASTM methodologies are possible for measuring sulfur content (Table 3). For the sake of enumerating the explicit properties of JP-5 it is reasonable to divide them into categories of safety, combustion efficiency, and maintenance issues. As might be expected, several properties of JP-5 have implications in more than one category. Color, being only an ambiguous measure of fuel quality, is not described any further.

Most of the properties of JP-5 are related to the fuel combustion efficiency. These include the cetane index, density, distillation profile, heat of combustion, hydrocarbon types, hydrogen content, smoke point, sulfur content, and thermal oxidation stability. Meeting these parameters insures that the fuel will ignite easily, burn completely, and meet emissions standards.

Several implicit properties for combustion efficiency can follow from the MILSPEC and ASTM descriptions. Implicit in the cetane index is the historical basis for calculations based on density and distillation profile. Cetane index may not be appropriate to calculate for fuels not derived from petroleum, although this has greater implications for diesel fuel and is discussed later. Similarly, both the fluorescent testing for hydrocarbon types and the smoke testing are associated with some aromatic content, while some pyrolysis and F-T fuels (discussed below) have zero aromatics content. The final implicit combustion property is that oxygenated fuels, especially if they contain no aromatics, may still meet the hydrogen content requirement of ≥ 13.4 wt-percent. This is probably not critical, however, because other properties such as heat of combustion, freezing point, and viscosity could still point to such a fuel issue.

Other properties are measured to maintain safe operations, including the flash point, freezing point, icing inhibitor content, kinematic viscosity, and water separation characteristics. The high flash point of $\geq 60^{\circ}\text{C}$ relates to shipboard operational safety, limiting the potential for fires onboard ships that carry aircraft. The other safety parameters relate to safety while airborne, such that fuel flow is not hindered by icing at the cold temperatures experienced at high altitude. There are no discernable implicit properties or issues regarding the jet fuel MILSPEC safety properties that would change with alternative fuels.

Maintenance issues are covered by several other properties of JP-5, although maintenance issues can certainly become safety issues, particularly for aircraft. These are acidity, copper corrosion, existent gum, particulate contaminants, smoke point, and water separation characteristics. Fuel filters will last longer when the existent gum, particulates, and water content are as low as possible. Engine parts such as turbine blades and fuel injectors will require less maintenance with a low corrosion and high smoke point fuel. As with the safety properties, there are no implicit properties of these determinations that are likely to be different with alternative fuels that otherwise meet the MILSPEC.

Table 3. MILSPEC requirements, standard testing methods, and explicit and implicit properties for JP-5.
Bolded ASTM methods are in common for analyses of F-76 (DFM).

Relevant Fuel Property	Value	ASTM Test #	Methodology	Implicit (I) and/or Explicit (X) Properties
Acidity	≤ 0.015 mg KOH/g	D3242	Standard test method	(X) Corrosion, seawater stability, salt fouling of turbines.
Cetane index	Report	D4737	Four variable equation	(I) Based on other measurements and an historical/empirical correlation. (X) Cetane affects starting, combustion, and emissions.
		D976	Estimated from gravity and mid-boiling point	
Color	Report	D6045	Automatic tristimulus method	(X) Very rough measure of quality.
		D156 ¹	Saybolt chromometer	
Copper corrosion	≤ 1 @ 100°C for 2 hours	D130	Copper strip tarnish test	(X) Measures corrosion and S “activity”.
Density	0.788-0.845 kg/L (36.0-48.0 API)	D1298	Hydrometer	(X) Affects cetane index and heat of combustion.
		D4052¹	Digital density meter	
Distillation profile	Report, range 205-300°C, 186-330°C for D2887, ≤ 1.5 wt-% loss, ≤ 1.5 wt-% residue	D2887	Gas chromatography	(I) Not relevant for biodiesel and some pyrolysis fuels. (X) Affects cetane index calculations and engine performance.
		D86¹	Atmospheric pressure distillation	
Existent gum	≤ 7.0 mg/L	D381	Jet evaporation	(X) Fuel filter service life.
Flash point	$\geq 60^\circ\text{C}$	D3828	Small scale closed tester	(X) Safety. Some effect on performance.
		D56	Tag closed tester	
		D93¹	Pensky-Martens closed cup	
Freezing point	$\leq -46^\circ\text{C}$	D2386 ¹	Standard test method	(X) Affects aircraft operability at altitude.
		D5972	Automatic phase transition method	
Heat of combustion	≥ 42.6 MJ/kg	D4809 ¹	Bomb calorimeter (precision method)	(X) Affects range and power.
		D3338	Standard test method	
		D4529	Standard test method	
Hydrocarbon types	≤ 25 vol-% aromatics	D1319	Fluorescent indicator adsorption	(X) Affects combustion and emissions.
Hydrogen content	≥ 13.4 wt-%	D3701	Continuous-wave low resolution NMR	(I) H content may be high even with high O (or water) content. (X) Affects combustion quality.

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Icing inhibitor content	0.10-0.15 vol-%	D5006	Standard test method	(X) Prevent fuel feed problems at altitude.
Kinematic viscosity	$\leq 8.5 \text{ mm}^2/\text{sec}$ @ -20°C	D445	Calculation of dynamic viscosity	(X) Affects storage, handling, and operational use of the fuel.
Particulate contaminants	$\leq 1.0 \text{ mg/L}$	D2276	Standard test method by line sampling	(X) Fuel filter service life.
		D5452 ¹	Laboratory filtration	
Sampling	According to standard practices, as appropriate	D4177	Standard practice, automatic method	No particular implications.
		D4306	Standard practice, for trace analyses	
		D4057	Standard practice, manual method	
Significant digit usage	According to standard practice	E29	Standard practice	No particular implications.
Smoke point	$\geq 19.0 \text{ mm}$	D1322	Standard test method	(X) Affects combustion quality. Correlates to hot turbine part lifetime.
Sulfur content	$\leq 0.30 \text{ wt-%}$	D1266	Lamp method	(X) Can effect performance, handling, processing, and emissions.
		D2622	X-Ray fluorescence spectroscopy	
		D4294 ¹	Energy dispersive X-ray fluorescence, 0.0150-1.0 wt-%	
		D4952	Doctor test (active sulfur)	
		D3277	Potentiometric method (mercaptan sulfur)	
		D5453	UV fluorescence, 0.00010-0.8 wt-%	
		D3120	Oxidative microcoulometry, 0.0003-0.1 wt-%	
Thermal oxidation stability	$\leq 25 \text{ mm Hg}$ pressure drop < 3 (tube deposit code)	D3241	JFTOT procedure	(X) Deposit decomposition products in fuel system @ high temperature.
Water separation characteristics	70-90 (MSEP rating, in min), depending on presence of additives according to Table II in MILSPEC	D3948	Portable Separometer	(X) Ability of fuel to release entrained/emulsified water. Affects icing.

¹ Refereed Method

Distillate Fuel Marine (DFM or F-76)

DFM is very similar to the commercially available products, marine gas oil and No. 2 diesel, but has tighter specifications for the cetane index and long-term stability. The issue of stability is inherent in the DFM name. Unlike what is permitted for marine gas oil and No. 2 diesel, DFM is a distillate, not a reformed or cracked, fuel. Reforming creates olefins (unsaturated hydrocarbons, Figure 1), which tend to form sludge and varnish (Batts and Fathoni 1991). DFM is the fuel normally used in internal combustion engines with compression ignition (diesel engines), but it can also be used as a land- or sea-based turbine fuel or for firing boilers (Stamper et al. 2007).

The parameters that DFM is required to meet are found in MIL-DTL-16884L. DFM can contain up to 5.8 mg/L N,N'-disalicylidene-1,2-propanediamine as a metal deactivator and 2-ethylhexyl nitrate as a cetane improver, as required. Although JP-5 and DFM have overlapping properties and many similarities, many of the properties that DFM and JP-5 share are more stringent for JP-5, including acidity, freezing point, hydrogen and sulfur contents, kinematic viscosity, and particulate contaminants (Table 4). Although turbine engines are generally fuel-flexible if used on land or sea, aircraft turbine engines rely on fuel that remains liquid at the low temperatures experienced at high altitudes. These more stringent values for JP-5 reflect the importance of a clean, low viscosity, low freezing point fuel necessary to keep turbine-engined aircraft aloft, and they are not important for diesel engines. Thus, kerosene-based fuel can be used in diesel engines, while diesel fuel cannot be used in aircraft engines.

Table 4. MILSPEC fuel properties shared by DFM and JP-5.

Relevant Fuel Property	JP-5 Value	DFM Value
Acidity	≤ 0.015 mg KOH/g	≤ 0.3 mg KOH/g
Cetane Index (calculated)	Report	43
Cloud/Freezing Point	≤ -46°C	≤ -1°C
Copper Corrosion	≤ "1" @ 100°C	≤ "1" @ 100°C
Density	0.788-0.845 kg/L	≤ 0.876 kg /L
Distillation Profile	Record initial boiling point, 10% point @ 205°C, Endpoint @ 300°C, ≤ 3.0 vol% loss+ residue	Record 10% and 50% boiling pts., 90% point @ ≤ 357°C, Endpoint @ ≤ 385°C, ≤ 3.0 vol% loss+residue
Flash Point	≥ 60°C	≥ 60°C
Hydrogen Content	≥ 13.4 wt-%	≥ 12.5 wt-%
Kinematic Viscosity	≤ 8.5 mm ² /sec @ -20°C	1.7-4.3 mm ² /sec @ 40°C
Particulate Contaminants	≤ 1.0 mg/L	≤ 10 mg/L
Sulfur Content	≤ 0.3 wt-%	≤ 0.5 wt-%

Implicit and/or Explicit Properties of DFM

DFM has 20 properties that must be determined and three standard practices that must be followed while measuring those properties (Table 5), and many of the properties can be measured by more than one technique. For example, the sulfur content of DFM can be measured by nine different methods, in comparison with the seven approved methods for JP-5. As with JP-5, the various important properties of DFM can be classified into categories of combustion,

safety, and maintenance issues. DFM has only one property that is clearly a safety issue – a flash point $\geq 60^{\circ}\text{C}$. The properties of flash point, color, and appearance will not be discussed any further.

Many of the specified properties of DFM pertain to combustion properties. These properties are cetane, density, distillation profile, hydrogen content, kinematic viscosity, and sulfur and hydrogen contents. Any petroleum-derived fuel meeting the diesel MILSPEC should behave appropriately in diesel engines. Several implicit properties of combustion parameters may not apply when non-petroleum fuels are tested, however. The cetane index (CI) is calculated according to the equation:

$$\text{CI} = 454.74 - 1641.416(\delta) + 774.74(\delta)^2 - 0.554(T_{50}) + 97.803(\log T_{50})^2 \quad (1)$$

where δ is the density (g/L) and T_{50} is the 50 percent distillation temperature ($^{\circ}\text{C}$). Lower density and higher T_{50} fuels will have a higher cetane index. This is an empirical relationship borne out by a long history of petroleum diesel and may not be appropriately applied to other fuels. For example, the distillation profile has been shown to be different (from petroleum diesel) for a diesel-like biofuel derived from pyrolysis (Adebanjo et al. 2005), making the validity of the cetane index from such fuels suspect. Calculating the cetane index of biodiesel is even more inappropriate, and the cetane number must be measured on a specialized test engine (Van Gerpen 1996). To resolve any difficulties, the cetane number for non-petroleum diesel fuel should be measured, rather than relying on a calculated cetane index. The remaining implicit combustion issue is that the hydrogen content can still be high, even with some oxygenated compounds. Unlike with JP-5, however, there is no MILSPEC requirement for a certain energy density for diesel fuel, even though performance and range are based on the energy density of the fuel. Determining the elemental composition might be useful in evaluating synthetic diesel fuel.

DFM has numerous properties that relate to maintenance issues. Engine maintenance issues like corrosion and/or carbon buildup can result from out-of-spec acid number, copper corrosion, trace metals content, ash content, and carbon residue. Cloud point, pour point, particulate content, storage stability, water and sediment, water separability are associated more with the fuel system maintenance issues, including filter and coalescer problems. Any of these issues, if ignored, have the potential to become safety issues, although the consequences are less than for aircraft turbine engines discussed previously. Implicit in determining the acid number is that the fuel being tested must be soluble in a mixture of toluene and isopropanol (Table 5). Alternative fuels that are not fully soluble may provide a misleading acid number. Another implicit issue is choosing the proper storage stability test. The accelerated method (ASTM D2274) is not reliable when testing cracked stock, because of the presence of olefins (Batts and Fathoni 1991).

Table 5. MILSPEC requirements, standard testing methods, and implicit and/or explicit properties of DFM.
Bolded ASTM methods are in common for JP-5 analyses.

Relevant Fuel Property	Value	ASTM Test #	Methodology	Implicit (I) and/or Explicit (X) Properties
Appearance	Clear, bright, and free of particulates at $\geq 25^{\circ}\text{C}$, or meets other requirements	D4176 ¹	Visual inspection	(X) General fuel quality (if clear).
Acid number	≤ 0.3 mg KOH/g	D974 ¹	Color-indicator titration	(I) Must be soluble in toluene/isopropanol
		D664	Potentiometric titration	(X) Affects corrosion.
Ash content	≤ 0.005 wt-%	D482	Standard test method	(X) Ash residue is metal compounds and/or other solids.
Carbon residue	≤ 0.14 wt-% on 10% distillation bottoms	D4530	Micro method	(X) Combustion chamber deposits. Detergents can increase the test result, yet actually decrease the actual combustion chamber deposits.
		D189	Standard test method (Conradson)	
	≤ 0.20 wt-% on 10% distillation bottoms	D524 ¹	Standard test method (Ramsbottom)	
Cetane	43 (index, calculated)	D976	Standard test method	(I) Based on other measurements plus historical record. (X) Engine performance.
	42 (number, measured)	D613 ¹	Standard test method	
Cloud point	$\leq -1^{\circ}\text{C}$	D2500 ¹	Standard test method	(X) Low temperature utility. Fuel filters clog at cloud point.
		D5771	Optical detection, stepped cooling method	
		D5772	Linear cooling rate method	
		D5773	Constant cooling rate method	
		D6371	Standard test method	
		IP 309	Institute of Petroleum method	
		D4539	Low-temperature flow test	
Color	≤ 3	D6045	Automatic tristimulus method	(X) Rough measure of quality.
		D1500 ¹	Standard test method	
Copper corrosion	≤ 1 @ 100°C	D130	Copper strip tarnish test	(X) Partial measure of sulfur “activity”.
Density	≤ 0.876 g/L	D1298¹	Hydrometer	(X) Affects cetane index and energy density calculations.
		D4052	Digital density meter	
Distillation profile	Record 10% and 50% points, 90% point @ $\leq 357^{\circ}\text{C}$, $\leq 385^{\circ}\text{C}$ endpoint ≤ 3.0 % loss+residue, by volume	D86	Atmospheric pressure distillation	(I) Not relevant for biodiesel and may not be appropriate for other alternative fuels. (X) Affects cetane index calculations and engine performance.
Flash point	$\geq 60^{\circ}\text{C}$	D6450	Continuously closed cup tester	(X) Safety.
		D93¹	Pensky-Martens closed cup	

Hydrogen content	≥ 12.5 wt-%	D4808	Low-resolution NMR spect.	(I) H content may be high even with high O (or water) content. (X) Affects combustion quality.
		D7171 ¹	Pulsed low-resolution NMR	
		D5291	Standard test method (CHN determination)	
Kinematic viscosity	1.7-4.3 mm ² /s @ 40°C	D445	Calculation, dynamic viscosity	(X) Affects storage, handling, and operation use of the fuel.
Particulate content	≤ 10 mg/L	D5452	Laboratory filtration	(X) Fuel filter service life. 10X higher limit than for JP-5.
		D6217 ¹	Laboratory filtration	
Pour point	$\leq -6^{\circ}\text{C}$	D5949	Auto. pressure pulsing method	(X) Low temperature utility. Fuel is “solid” below pour point.
		D5950	Automatic tilt method	
		D5985	Rotational method	
		D97 ¹	Standard test method	
Synthetic seawater	According to standard practice	D1141	Standard practice	No particular implications.
Sampling	According to standard practice	D4177	Standard practice (automatic)	No particular implications.
		D4057	Standard practice (manual)	
Significant digit usage	According to standard practice	E29	Standard practice	No particular implications.
Storage stability	≤ 3.0 mg/L	D5304 ¹	Oxygen overpressure	(I) D2274 is not reliable for cracked stock. ² (X) Relative storability $\pm$ additives measures insolubles formed during (simulated) storage.
	≤ 1.5 mg/L	D2274	Accelerated method	
Sulfur content	0.5 wt-% Method used depends on expected range, according to MILSPEC	D1266	Lamp method	(X) Can effect performance, handling, processing, and emissions.
		D129	General bomb method	
		D1552	High temperature method	
		D2622	X-Ray fluorescence spect.	
		D4294 ¹	Energy dispersive X-ray fluor.	
		D7039	Monochr. wavelength dispersive X-ray fluor. spect.	
		D5453 ¹	UV fluorescence	
		D6920	Oxidative combustion	
		D3120	Oxidative microcoulometry	
Trace metals content	≤ 1.0 ppm Ca and Na+K ≤ 0.5 ppm Pb and V	D3605 ¹	Atomic abs. and flame emission spectroscopy	(X) Oil soluble metal content affects corrosion of engine.
		D7111	ICP-AES	
Water and Sediment	≤ 0.05 vol-%	D2709	Centrifugation	(X) Water, microbial growth, and formation of sediments are related
Water separability	≤ 10 min at 25°C	D1401	Standard test method, uses D1141 synthetic seawater	(X) Affects microbial growth and sediment formation

¹ Refereed Method² Batts and Fathoni 1991.

Lubricity of DFM

Issues related to fuel lubricity became apparent with the battlefield usage of kerosene fuels in diesel engines, resulting in fuel pump and fuel injector problems (Lacey and Westbrook 1997; Stavinoha et al. 2004). F-T fuel has similarly been demonstrated to have low lubricity and can cause premature fuel pump wear and failure (Frame and Alvarez 2003). Proprietary additives are available that enhance fuel lubricity (Frame and Alvarez 2003; Lacey and Westbrook 1997). Although this report treats the lubricity of DFM as an implicit property, a future MILSPEC will have an explicit standard for lubricity (Williams and Chang 2008).

Several lubricity tests are available for evaluating fuel lubricity: the Ball-On-Cylinder Lubricity Evaluator Test (BOCLE, ASTM D5001), the Scuffing Load BOCLE Test (SLBOCLE, ASTM D6078), and the High Frequency Reciprocating Rig Test (HFFR, ASTM D6079). The BOCLE test measures the wear scar of a ball on cylinder under light load. The SLBOCLE test measures the load required for metal-to-metal contact and scuffing. The computer-controlled HFFR test method evaluates boundary lubrication properties of a ball against a flat surface, with minimal effect of viscosity on the measurement. The three tests do not necessarily correlate with each other, but certain values are predictive of lubricity-based problems that are likely to occur in equipment (Frame and Alvarez 2003; Lacey and Westbrook 1997).

Alternative Fuels

The alternative fuels discussed in this report are pyrolysis, F-T, and biodiesel. The terms pyrolysis and F-T fuels can be used to describe several very different liquid fuels, some of which are more similar to petroleum fuels than others, and with different levels of suitability for use in marine diesel engines. Unfinished (raw) F-T or pyrolysis fuels are unsuitable, whereas finished fuels are more likely to be suitable.

Pyrolysis Fuels

Pyrolysis, or thermal degradation, of carbonaceous material under various (typically anaerobic: O₂-free) conditions can be used to produce gaseous, liquid, and/or solid fuels. Coal and biomass are common pyrolysis substrates, but typically with different goals for the products. Pyrolysis of coal is done to produce coal gas (a mix of hydrogen, carbon monoxide, methane and other flammable gases), coal tar (heavy hydrocarbons), and coke (carbon). Pyrolysis of biomass has the goal of producing wood gas (equivalent to coal gas), liquid fuel, and/or charcoal. Liquid fuels are preferred for transportation due to the ease of delivery and use. A high energy density is also preferred, consistent with current petroleum-derived fuels.

In considering liquid fuel production from biomass, there are two major classes of biomass. The largest source of biomass is material from plants: grasses, wood, bark, and agricultural residues such as corn stover and straw. Plant materials are composed primarily of lignocellulose, a complex polymer composed of varying portions of lignin, cellulose, and hemicellulose polymers. Lignin is a polymer formed from several methoxy-substituted phenols, with a generalized formula of C₉H₁₀O₂ (OCH₃)_{0.9-1.4}. It composes 5-30 percent of the dry weight of plants (Larsson et al. 2001). Cellulose, a β-glucose homopolymer, makes up 35-50 percent of plant dry weight. Hemicellulose is a copolymer of 5- and 6-carbon sugars, with the 5-carbon sugar xylose being predominant. Hemicellulose comprises 20-35 percent of plant dry weight (Lynd et al., 2002). An important characteristic of lignocellulose is its high oxygen content, 26-

28 wt-percent (dry). The second, although less abundant, main source of biomass is slaughterhouse waste (termed offal), consisting of a large proportion of fatty material. The 10-12 percent oxygen content of fatty material (McCormick et al. 2001) contrasts with 26-28 wt-percent oxygen content of lignocellulose, resulting in a more petroleum-like product when pyrolyzed.

Pyrolysis Fuel from Plant Materials

Most processes for liquid fuel production focus on plant material, since it is the most abundant source of biomass. Several reviews of lignocellulosic material pyrolysis are available (see Oasmaa and Czernik 1999; Czernik and Bridgewater 2004; Mohan et al. 2006; Elliot 2007). In this report, the fuel from pyrolysis of plant biomass will be called lignocellulosic pyrolysis fuel (LPF).

The most common method, fast pyrolysis, relies on the water content of lignocellulose and rapid (<10 sec) heating and quenching of biomass particles. Mohan et al. (2006) review several varieties of fast pyrolysis technologies such as flash-liquid, flash-gas, ultra, and vacuum pyrolysis. A second method, distinguished from the first by taking minutes to hours to process, is slow pyrolysis. The product from slow pyrolysis is similar to that from fast pyrolysis, but with a slightly lower oxygen content (Elliot 2007). In a third method, hydrothermal pyrolysis, biomass and additional water are pressurized and heated, resulting in a “heavy oil” fraction and an aqueous fraction (Elliot 2007; Xu and Lad 2008). Pressurization with carbon monoxide (CO) decreases the oxygen content of the heavy oil. The heavy oil has an energy density of 30-35 MJ/kg and the aqueous layer has about a 50 percent lower energy content. The heavy oil is more amenable than bulk LPF for upgrading by hydrotreatment (described later).

Bulk LPF is a complex emulsion or colloid of water, furancarboxaldehydes, pyrones, carboxylic acids, hydroxylaldehydes, hydroxyketones, sugars, phenolics, and phenolic oligomers (Ba et al. 2004a, 2004b; Chaala et al. 2004). Notably, the product typically contains 45-50 wt-percent oxygen (including water). The bulk LPF can be fractionated by addition of excess water and gravity separation, resulting in an aqueous layer and a heavy oil fraction, approximating those fractions from the hydrothermal pyrolysis. The heavy oil LPF is less acidic, less polar, and has much less water (~5 percent vs. up to 30 percent) than bulk LPF, but with a yield of about 20 percent of the total energy value of the starting material (Mohan et al. 2006). Neither bulk nor heavy oil LPF will dissolve in hydrocarbon solvents. In fact, hydrocarbons are essentially undetectable in the products of pyrolysis performed at $\leq 538^{\circ}\text{C}$ (Zhang et al. 2007). The properties of LPF are shown in comparison to several other fuels in Table 6.

Serious problems with LPF are numerous, and include the low heating value, high water content, corrosivity to copper and aluminum (Darmstadt et al. 2004), high molecular weight (affecting the volatility and viscosity), aging stability problems, phase stability, and the fact that LPF is not distillable (Oasmaa and Czernik 1999). Since it decomposes upon distillation, upgrading bulk LPF is difficult. The heavy oil fraction of LPF is more stable and can be upgraded, but given the relatively low yield and the very high oxygen content (relative to petroleum), this may not be economical. If heavy oil LPF were to be upgraded by hydrotreating, the high aromatic content (from the phenolic constituents) probably makes it a better replacement for gasoline than for diesel or jet fuel.

Table 6. Comparison of the basic physical properties of JP-5, DFM, biodiesel, pyrolysis, and F-T fuels. Properties underlined in red do not meet specifications for JP-5 and/or DFM.

Physical Characteristic	JP-5 ^A	DFM ^C	Biodiesel	LPF ^{H,I}	FPF ^J	Finished F-T or Pyrolysis Fuels ^{L,M,N,O}
General Formula	C ₈ -C ₁₆ ^B	C ₁₀ -C ₂₂ ^B	C ₁₈ H ₃₆ O ₂ ^D	C ₁₀ H ₁₉ O ₇ (≤ 30% H ₂ O)	C ₁₀ H ₂₀ O (≤ 5% H ₂ O)	C ₈ -C ₂₀ , as specified
Density (g/mL)	0.788-0.845	< 0.876	<u>0.88</u> ^D	<u>1.2</u>	<u>0.86-0.88</u>	<u>0.76 – 0.78</u>
Energy Density (MJ/kg)	≥ 42.6	~44 typical ^L	<u>38</u> ^E	<u>15-19</u>	<u>39-40</u>	43.6-44.1
Volumetric Energy Density (MJ/L, nominal)	35.3	40.4	<u>32.9</u> ^E	<u>19.2-22.8</u>	<u>35.2</u>	34.0
Cetane (index or number)	Report	≥ 43 index	≥47 number ^D	<u>Requires cetane improvers</u>	46-54 index	62 index to 75 number
Flash Point (°C, open cup)	≥ 60	> 60	≥ 93 ^F	64	Not reported	49-62
Melting Point (°C)	≤ -46	≤ -1 (cloud point)	<u>-3 to +19</u> ^G (pour point)	-33 (pour point)	Not reported	-59 to -50
Boiling Point (°C)	205-300	200-385	360 ^F	<u>Decomposes, ≤ 50% residue</u>	<u>170-550</u>	As specified 182-280 ^N
Viscosity (cSt)	8.5 (max) @ 20°C	1.7-4.3 @ 40°C	1.9 – <u>6.0</u> @ 40°C ^D	<u>25-1000</u> @ 20°C	<u>4.5-22</u> @ 40°C	2.7 @ 40°C 4.6-7.0 @ -20°C
Acidity (mg KOH/g)	< 0.1	< 0.3	<u><0.5</u> ^F	<u>48-83</u>	Not reported	0.001
Aromatics (wt-%)	≤ 25	~ 25-35	0	Not reported	0-30 ^K	< 0.1 – 1.4
Hydrogen Content (wt-%)	≥ 13.4	≥ 12.5	12.7	<u>≤ 10</u>	12.5, est.	15.1 – 15.3

^A MIL-DTL-5624U: Mil-spec for JP-5

^B www.chevron.com/products/prodserv/fuels

^C MIL-DTL-16884L: Mil-spec for DFM

^D National Biodiesel Board, 2007, Weight&Formula.pdf

^E National Biodiesel Board, 2007, BTU_Content_final.pdf

^F ASTM D6751-06B

^G Biodiesel Handling and Use Guidelines, Department of Energy, 2006

^H Mohan et al.2006

^I Oasma et al. 2005

^J Adebajo et al. 2005

^K Katekaneni et al. (1995) w/reforming catalysts

^L Wu et al. 2007

^M Corporan et al. 2007

^N Lamprecht 2007

^O Frame and Alvarez 2003

Engine Testing with LPF

Although LPF is has little in common with to petroleum fuel, strictly speaking, it is combustible and can be used as a fuel. Diesel engines can run on it, given modifications to the fuel delivery system and addition of ignition improvers (Oasmaa et al. 2005; Shihadeh and Hochgreb 2000). Even with modifications, injector coking and low energy density are problematic for usage of LPF. Turbine engines are also able to burn LPF, with similar problems. Coking of fuel nozzles, and formation of deposits in the combustion chamber and on turbine blades are all significant problems. LPF is somewhat more suitable for firing boilers, especially when co-fired with petroleum fuel and as long as a separate fuel delivery system is maintained for each fuel (Czernik and Bridgewater 2004).

Although specially-modified experimental engines can be contrived to run on LPF, it should not be considered a suitable substitute for petroleum-derived fuels. Moreover, it is insoluble in petroleum products like diesel fuel, jet fuel, and gasoline. Because the properties of

LPF are so fundamentally incompatible with the existing petroleum infrastructure, it is unlikely that such fuels could find their way into U.S. Navy fuel stocks.

Pyrolysis Fuel from Fatty Materials

Pyrolysis of fatty materials results in a material very different from LPF. Vegetable oil, animal fat, and animal carcasses (offal) are all suitable substrates, although biodiesel production does compete for animal fat and (especially) vegetable oil as feedstocks. Fats and oils are composed of three fatty acids esterified to glycerol. The majority of the fatty acids in fats and oils are 16 or 18 carbons in length, either saturated, monounsaturated, or polyunsaturated (Adebanjo et al. 2005). A main difference between fatty materials and lignocellulosic materials is that fats contain only ~10-12 percent oxygen, compared with the 29-49 percent oxygen in lignocellulose (~29 percent O in lignin and 49 percent O in hemicellulose and cellulose). In addition, fragmentation of lignocellulose results in a large variety of compounds, including large ($M_r > 1000$) oligomers. In contrast, the fragmentation of fats necessarily results in molecules smaller than 20 carbons in length. Analogous to LPF, although at the risk of the two fuels sounding too similar to each other, this document will use the nomenclature fatty pyrolysis fuel (FPF) for the liquid product from pyrolysis of fatty material. The strategic importance of this process is demonstrated by the fact that the annual supply of offal in the U.S. could be converted into 50 million barrels of pyrolysis fuel, or 150 percent of the current Navy fuel needs (Bergeron et al. 2007).

In a process that has been recently commercialized by Changing World Technologies, turkey and pork waste are converted into a petroleum-like product. The offal is chopped, pressurized and heated. The water is flashed off at a lower pressure and the remaining material is repressurized and reheated. An aqueous fraction and an oily fraction are separated by centrifugation. The company claims a process energy efficiency of 85 percent and a product that is “chemically similar to a mixture of diesel and gasoline” and “better than crude” (Lemly 2006; Renner 2003). The double processing allegedly improves the process efficiency, but details are not publicly available, making claims about this product very difficult to evaluate.

Several more detailed reports are available for FPF production, however. Pyrolysis of lard at 600°C resulted in 33-41 percent gaseous products and 49-61 percent liquid products (Adebanjo et al. 2005). Measured parameters for the liquid product are entered in Table 6, and are similar to diesel, except for a lower energy density (40 MJ/kg vs. 45 MJ/kg) and higher viscosity. Both parameters were related to the oxygen content of the liquid product which, as the authors suggest, could be mitigated by hydrotreating. In another report, Katikaneni et al. (1995) demonstrated a 40-50 percent liquid yield from pyrolysis of Canola oil at 400-550°C over catalysts. The liquid product consisted of ~10 percent oxygenated compounds, ~30 percent aromatics, ~15-20 percent paraffins, and 30-45 percent unidentified products. The relatively high aromatic yield was based on reformation of paraffins and olefins by the catalysts (noted in Table 6). Steam reforming increased the yield of olefins, but kept the catalysts cleaner.

Pyrolysis experiments combining lignite (a low-grade variety of coal) and safflower seed (an oilseed) found a synergistic yield of liquid product (40 percent) at 5 percent coal (Onay et al. 2007). This synergy was believed to be due to catalysis by the minerals in the coal. The liquid product was approximately 10 percent aromatic, 85 percent aliphatic, and 5 percent oxygenated compounds, with > 60 different compounds identified by gas chromatography/mass spectroscopy. In this case, much of the aromatics content was reasoned to be derived from the coal.

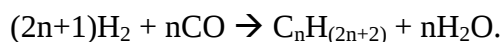
Engine Testing with FPF

None of the several reports cited earlier involved any engine testing, so the suitability of FPF as an alternative diesel fuel remains unknown. However, those reports did provide detailed product information indicating that FPF is much more similar to petroleum than is LPF, as it contains a wide range of hydrocarbon compounds and much less oxygen and water. Given that LPF could be made to burn in a diesel test engine, it is reasonable to think that FPF should be less problematic. More relevant to this report, FPF is more easily upgraded using standard petroleum refining techniques.

Raw FPF should be very similar to raw F-T fuel, described below, except that the molecular weight and distillation range of FPF is probably smaller. Raw FPF (like raw F-T) does not meet the MILSPECs for either JP-5 or DFM, however (Table 6). Further processing of FPF by hydrotreating (Adebanjo et al. 2005) and/or extraction of polar compounds (Ward et al. 1951) would upgrade raw FPF and improve its properties. Hydrotreating is used to remove oxygen, sulfur, and nitrogen, as well as saturating the carbon-carbon double bonds of olefins. Whether derived from petroleum or biomass, any significant amount of olefins in the final product will likely contribute to storage problems.

Fischer-Tropsch (F-T) Fuels

F-T fuel production begins with the complete gasification of organic material. Gasification by hydrolysis and/or partial oxidation of carbonaceous material occurs at higher temperatures than pyrolysis, converting that material into syngas, a mixture of hydrogen and carbon monoxide ($H_2 + CO$). Since any carbonaceous material can be converted into syngas, organic material such as plant and animal residues (waste) can be used, although coal or natural gas are the more typical feedstocks. Sulfur is removed from syngas prior to the F-T process, so the resulting F-T fuel contains essentially zero sulfur. F-T reactions are multi-step, requiring multiple passes over the catalysts. The exothermic ($\Delta h = -165 \text{ kJ/mol CO}$) F-T synthesis reaction is simplified as:



The technology for F-T fuel production is fairly mature, having seen use by Germany and Japan in World War II and South Africa up to the present (Bergeron et al. 2007; Sliepcevich et al. 1977). Japan, and especially Germany, relied heavily on F-T fuel during World War II, because they could not acquire sufficient petroleum for their war efforts. South Africa relied on the F-T process from the Sasol Company to make much of its liquid fuel during the apartheid era. Thus, in these cases, the political situation favored the production of F-T fuel.

The production of F-T fuels is viewed as strategically important in many countries with limited petroleum, but abundant coal, natural gas, and/or biomass resources. Chevron, Choren, Shell Oil, and Sasol are involved in various F-T projects in Indonesia, China, Qatar, and the U.S. (Bergeron et al. 2007). In the absence of political considerations, the economic feasibility of these projects is primarily dependant on the price of petroleum (Sichinga 2006). Given petroleum price volatility, F-T fuel suppliers would prefer to make the large capital investments that are necessary only if long-term price guarantees could be provided (Brown, 2006).

The DoD “Synthetic Fuel Initiative” lists a long-term requirement of 110,000 barrels per day of synthetic fuel, for blending 50/50 with petroleum fuel (DESC 2007). Consistent with the “Assured Fuel Initiative” from the Office of the Secretary of Defense, the Air Force has been studying the use of a (JP-8-like) F-T fuel produced from natural gas by the Syntroleum

Corporation (Woodbury 2006, DESC 2007). Based on these tests, the B-52 has been certified to fly using 50 vol-percent F-T fuel. The Air Force plans to have every airframe certified to fly on this F-T/JP-8 blend by 2011 (Hernandez 2007). As of April 2008, the JP-8 MILSPEC permits blending with up to 50 percent F-T fuel (meeting specifications outlined in Appendix A of MIL-DTL-83133F).

Raw F-T Products

Although the simplified reaction shown above shows only the production of paraffins, raw F-T fuel, sometimes termed “syncrude” (Suppes et al. 1998), is actually a complicated mixture of products. Raw F-T product primarily contains paraffins (70-75 percent), but also includes unsaturated hydrocarbons (olefins, 10-15 percent) and oxygenated compounds (5-15 percent alcohols, ketones, aldehydes, and acids). Aromatics, unless appropriate cracking catalysts are used, are scarce (DiSanzo 1981; Sliepcevich et al. 1977; Spath and Dayton 2003). A range of very low to very high molecular weight products (gases to waxes) results from F-T synthesis. Given the wide range of products, particularly the C₂₀₊ waxes, raw F-T is not suitable directly as a fuel, but must be processed further (Suppes et al. 1998), analogous to crude petroleum.

Finished F-T Fuel

Raw F-T fuel is typically upgraded, depending on the intermediates and according to the final desired product. This report considers raw F-T and FPF to be equivalent, such that either can be upgraded to a finished fuel. Table 6 shows a small range of finished F-T products in the kerosene-to-diesel range, although other product ranges and compositions are possible. Depending on demand, the heavier waxes can be hydrocracked to produce additional material in the liquid range for kerosene and diesel fuels (de Klerk 2007). Two broad types of F-T fuel are possible 1. typical, low-aromatic F-T fuel and 2. high-aromatics F-T fuel. Aromatics-rich F-T fuel, useful as gasoline, can be produced by a high temperature process or cracking (Fernandez 2006; Kahandawal et al. 2004; Lamprecht et al. 2007). Short, low-boiling point olefins can also be thermally upgraded into heavier products by crosslinking (de Klerk 2005). Distillation of the product over the desired temperature range is standard practice in achieving all finished fuels, including those produced by the F-T process (Lamprecht, 2007).

The low aromatics and sulfur content of typical F-T fuel makes it suitable for blending with stocks that might otherwise be unacceptable for certain uses. Coal liquefaction products are very rich in aromatics, polyaromatics, and sulfur (Gül et al. 2006; Kahn 1988; Smith and Bruno 2007; Song et al. 1992). By blending with low-aromatics and sulfur-free F-T fuel, such products can be upgraded (O’Rear et al. 2004; Cookson and Smith, 1992). Similarly, high-aromatics F-T fuel can be blended with low-aromatics F-T fuel, affording some fuel system elastomer protection and a higher volumetric energy density (Lamprecht et al. 2007). Alternatively, o-rings and similar seals that are compatible with low-aromatics fuels can be used.

Engine Testing with Finished F-T Fuel

In a broad sense, the long history of commercial and military use of F-T fuels, particularly in South Africa, lends a great degree of confidence to the general suitability of such fuel in current U.S. Navy marine diesel engines. The compatibility of F-T fuel for storage with seawater contamination is less well known, and can be problematic. This issue is currently under investigation in our, and other, laboratories.

The differences in properties between F-T and petroleum diesel fuels can affect engine performance. F-T fuel has a 2.7% higher gravimetric energy density (Wu et al. 2007) and engine thermal efficiency (Abu-Jrai et al. 2006). Based on the lower density of F-T fuel (Table 6), however, the volumetric energy density will be lower than for diesel. The maximum combustion pressure and peak heat release rate, properties that affect both performance and emissions, are 2.9 and 2.8 percent lower for F-T fuel (Wu et al. 2007).

The lower density of typical F-T fuel may be an issue for marine diesel engines. Given a fixed fuel tank size, power and/or range based on F-T fuel will be reduced relative to diesel fuel. With an average diesel density of 0.836 (Westbrook and LePera 1999) and an average F-T density of 0.77 (Table 6), the volumetric energy density of F-T is 14% lower than diesel, even though the gravimetric energy density of F-T is 2.7% higher (Wu et al. 2007). If the single battlefield fuel is kerosene-based, however, power and range are already compromised. The penalty for using F-T fuel rather than kerosene is smaller, since kerosene is already less dense than diesel because of lower aromatics content (Table 6). Specifying a higher density F-T fuel, *i.e.* richer in aromatics, could mitigate this.

The differences in properties between F-T and petroleum diesel fuels can affect engine emissions. Commonly, emissions of NO_x and particulates are decreased when diesel engines burn F-T fuel (Abu-Jrai et al. 2006; Clark et al. 1999; Wu et al. 2007; Suppes et al. 1998; Szybist et al. 2005). Particulate emissions correlate to aromatic and polyaromatic content, which are much lower in F-T fuel than in diesel fuel (2 vs. 25-35 wt-percent, Wu et al. 2007). The lower NO_x emissions afforded by F-T fuel are related to its ignition properties. The higher cetane index/number of F-T fuel affects ignition, as does its bulk modulus. With F-T fuel, mechanical ignition can be retarded because of a lower bulk modulus, which affects fuel injection timing (Abu-Jrai et al. 2006; Boehman et al. 2004). High-pressure, common rail systems with electronically-controlled fuel injection should not be affected by bulk modulus of the fuel. Fuel-injection timing can be optimized for the low bulk modulus and high cetane of F-T fuel (Abu-Jrai et al. 2006; Suppes et al. 1998).

Biodiesel Fuel

Biodiesel is produced by the transesterification of fats. Individual fat molecules are composed of three fatty acids esterified to glycerol. Transesterification of fat replaces the glycerol with another alcohol, typically methanol. The transesterification product is a mixture of methyl esters of fatty acids and free glycerol. The glycerol and any free fatty acids are separated by water washing and the hydrophobic fatty acid methyl esters are biodiesel.

Proponents of biodiesel have said that the diesel engine requires little to no modification to be able use biodiesel and various blends with petroleum diesel. Biodiesel has been tested in diesel engines and shows promise as an alternative fuel because it reduces particulate and carbon monoxide emissions and is more biodegradable than petroleum diesel, if spilled. It has the potential of reducing the United States dependence on foreign oil imports. Biodiesel is more expensive to produce than petroleum diesel and has a lower energy content, however, meaning lower mileage and/or less power at a higher cost. In the United States, biodiesel is derived primarily from soybean oil and is in direct competition with using soybean as a food source. Higher prices for soybean and other grains are expected as more of the soybean crop is converted into biodiesel.

Properties specified in ASTM D6751 - 06b are measured to qualify the fuel as biodiesel. Several of these measurable or explicit properties are directly linked to the diesel engine

performance, which lead to other measurable or implicit properties of the fuel. These implicit properties are not specified in the above standard, but are important in the understanding of the atomization and combustion characteristics of the biodiesel. The goal of this section is to compare the explicit properties of biodiesel with petroleum diesel from their respective standards and to identify and quantify the implicit properties that effect on the performance of the diesel engine.

A comparison of the physical and chemical requirements for DFM and biodiesel is presented above in Table 6. Biodiesel specifications are taken from the ASTM biodiesel standard (D6751-06b), which is less strict than the DFM standard. On several specifications, biodiesel does not meet the DFM MILSPEC. Notably, biodiesel is more dense, less energy dense, has a higher melting point and viscosity range, and can be more acidic than petroleum diesel. Although biodiesel does not meet MILSPEC, it is in wide use as blends with petroleum diesel, which provides a high likelihood of exposure to the Navy.

Engine Testing with Biodiesel Fuel

There are a few explicit properties such as flash point and viscosity and additional properties of the fuel that were found to be correlated with the implicit properties associated with the atomization and combustion characteristics. An experimental study was done to determine the atomization and combustion characteristics of biodiesel blends with petroleum diesel (Lee et al. 2005). Physical properties such as kinematic viscosity and surface tension of the biodiesel mixture were found to correlate with spray atomization characteristics measured as spray tip penetration, mean size distribution diameter (Sauter Mean Diameter¹), mean velocity distribution, and mass flow rate distribution. The cetane number and spray atomization characteristics play a role in the combustion characteristics of combustion pressure, ignition delay, and rate heat release for a single cylinder engine. For the combustion measurement, the injection timing and injection pressure were also varied and found to affect the combustion characteristics.

Viscosity and surface tension increase with increasing concentration of biodiesel in the blends. These results showed that the atomization droplet size (Sauter Mean Diameter) for the biodiesel, derived from unpolished rice oil and soybean oil, was larger than petroleum diesel (Lee et al. 2005). The droplet size of petroleum diesel is more uniform than biodiesel blends over the injection period. The larger droplet size is attributed to the higher viscosity and surface tension of biodiesel than petroleum diesel. The initial mean velocity of the petroleum diesel is higher than the biodiesel blends. The trend reverses at injection time greater than 1 msec. The atomization characteristics of biodiesel appear to create localized areas of higher fuel concentration. This result may require some thought in the redesigning the nozzle to get more uniform droplet size by accounting for higher viscosity and surface tension in the biodiesel blends to achieve better fuel to air mixing.

The bulk modulus of biodiesel is greater than petroleum diesel (Boehman et al. 2003, 2004). A higher bulk modulus means that biodiesel is less compressible and has a higher speed of sound, which can affect the delivery of the fuel by pressure actuation through the pipes and nozzles of the injection systems. The injection timings of the biodiesel blends are occurring earlier than petroleum diesel. The spray development profiles of the biodiesel (soybean based) blends appear broader near the tip ends of the profiles than the petroleum diesel. The spray tip penetration results were similar for all the different fuels. The injection (mass flow) rate profiles

¹ Sauter Mean Diameter is the surface area moment mean, which is the ratio of the sum of the surface volume to the sum of the surface area.

of biodiesel blends (10, 20, and 40 percent) for fixed quantity of fuel (8 mg) are dependent on the injection pressure. The results showed that the peak injection rate decreases with increasing concentration of biodiesel in the blends. The increase in friction between the nozzle surface and biodiesel may be the cause for the reduction in injection velocity and peak injection rate. The injection pressure may have to be increased for biodiesel blended fuels to achieve a desired mass flow rate profile.

The combustion characteristics of a diesel engine are determined by measuring the cylinder pressure and the rate of heat release. The cylinder pressure characterizes the ability of the fuel to mix well with air (the atomization characteristics) and burn. The rate of heat release is dependent on the burn rate and the heat value of the fuel. These combustion characteristics are demonstrated in two diesel engine tests beds. The first test bed was a single-cylinder engine with a common rail injection system (Lee et al. 2005). The engine was operated at 1000 rpm and coupled to a DC dynamometer. The second test bed was a four-stroke, four-cylinder engine (Sinha and Agarwal 2007). Measurements were made at two engine speeds: 1400 and 1800 rpm at no engine load. These measurements were repeated at 50 and 100 percent of engine rated load for the two engine speeds. The engine test conditions used by Sinha and Agarwal (2007) are representative of a diesel engine in use, while the conditions used by Lee et al. (2005) may have been dictated by limitation of the single-cylinder engine.

The limited results of Lee et al. (2005) were in agreement with Sinha and Agarwal (2007) only under a specific engine condition: at no engine load. Under this condition, both studies found that the ignition delay decreases as the concentration of biodiesel in the blends increases and the peak pressure is higher for the biodiesel blends than diesel.² Each study offered a different explanation for the above results. Lee et al. (2005) reasoned that the lower ignition delay was due to the higher cetane number of biodiesel and the higher peak pressure was due to the promotion of the combustion by oxygen in the biodiesel. Sinha and Agarwal (2007) reasoned that the shortened ignition delay may also be due to the higher cetane number. They offered an additional explanation that biodiesel may undergo thermal cracking, generating low molecular weight compounds that can be ignited earlier. The high peak pressure of biodiesel was greater than diesel was attributed to the combustion of the biodiesel blends occurring earlier and near top dead center (TDC). As the engine load was increased, the combustion starting points were similar for all the fuels, indicating a reduction in the ignition delay. This leads to a reversal in the peak pressure trend, the peak pressure for diesel was greater than biodiesel as the engine load increased. Also, the peak pressure was independent of the engine speed.

The peak maximum of the instantaneous rate of heat release increased as the concentration of biodiesel in the blends increases (Lee et al. 2005). The peak maximum of the instantaneous heat release of diesel was the lowest. This trend was reversed in the results by Sinha and Agarwal (2007). The peak maxima of the instantaneous rate of heat release were greater for diesel than the biodiesel blends. They reasoned that the higher volatility of the diesel and better mixing of the diesel with air produced a greater heat release than the biodiesel blends. The better mixing of diesel can be attributed to the atomization characteristics: smaller droplet size and greater tip penetration as previously discussed.

The cumulative heat release (Sinha and Agarwal 2007) for the biodiesel blends shows an earlier release of fuel energy at the lower engine loads. Combustion for diesel starts later but it

² D100 and B0 are for 100 percent diesel fuel, BD10b and B10 are for a blend of 10 percent biodiesel to 90 percent diesel, BD20b and B20 are for a blend of 20 percent biodiesel to 80 percent diesel, BD40b is for a blend of 40 percent biodiesel to 60 percent diesel, and B100 is for 100 percent biodiesel.

quickly exceeds the cumulative heat released for biodiesel blends, suggesting a faster burn rate of diesel. The cumulative heat release decreases as the proportion of biodiesel increases in the blend, owing to the lower heating value of the biodiesel.

Biodiesel as an additive in marine fuels can be particularly problematic, given that some fuel is stored in seawater-compensated tanks, for ballasting purposes. In such tanks, as fuel is pumped for use, seawater is added to compensate for the decrease in volume and mass. Mushrush et al. (2005) describe problems with biodiesel exposure to seawater that include fuel instability, water separation problems, and filter plugging. Fuel not stored with exposure to seawater should not face the same problems, but this must be a serious consideration for the U.S. Navy. Because of such problems, recent regulations (COMNAVSEASYS COM 051749ZJUN08) prohibit biodiesel blends onboard US Navy ships.

Improving Alternative Fuels

Because LPF, FPF, and raw F-T explicitly cannot meet MILSPECs for either DFM or JP-5, the implicit properties of DFM and JP-5 have no bearing on the suitability of these unfinished alternative fuels. They are unsuitable for military use to such a degree that they should not be any concern. Of these unfinished fuels, FPF and raw F-T can be upgraded to a petroleum-like product with minimal difficulty, whereas LPF cannot.

Finished F-T fuel and FPF should meet the explicit properties of the DFM MILSPEC. Biodiesel may not or will not meet several properties in the MILSPEC, notably the acidity, pour point and storage stability (including water contamination). Finished F-T fuel can be produced that will meet the MILSPEC, but can still have properties that may be problematic for use in marine diesel engines. The contrasting bulk modulus issues with biodiesel and finished F-T fuel are simply mitigated by using a high-pressure, common-rail fuel injection system rather than fuel injection triggered by a mechanical pump. The implicit problems posed by biodiesel and F-T fuels are summarized below (Table 7).

Many problems stemming from the use of alternative fuels will be mitigated by using alternative fuels as blends, including the lower volumetric energy density of finished F-T and biodiesel fuels. On one hand, 100 percent biodiesel is much more different from diesel than is F-T fuel. However, this is mitigated by the likelihood that biodiesel at ≤ 5 -20 percent is much more common than 100 percent biodiesel. On the other hand, even though F-T is more like petroleum diesel, F-T might be more problematic than biodiesel, because it is more likely to be available at a higher percentage. The lubricity of F-T blends at 50 percent with kerosene, tested and certified by the Air Force, is problematic. If it is to fuel diesel engines as a single battlefield fuel, the low lubricity of such a blend must be managed. Both the low lubricity of F-T fuel and the storage stability of biodiesel could be addressed by additives, but water contamination of biodiesel blends remains a problem.

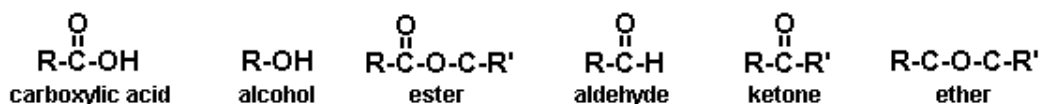
Table 7. Summary of implicit problems of alternative fuels and possible solutions.

Alternative Fuel	Relative to Diesel	Problem	Solutions
Finished F-T	Low volumetric energy density	Less power and/or range	Blend with diesel and/or high-aromatics F-T
	Some elastomer shrinkage	Seals can leak	Blend with diesel and/or high-aromatics F-T Use compatible elastomers
	Low lubricity	Premature fuel pump and fuel injector failure	Lubricity additives
	Low bulk modulus	Retarded injection timing	Use common-rail fuel injection
Biodiesel	Poor seawater and microbial stability	Filter plugging, fuel stability	Avoid seawater contamination (may not be possible)
	Low energy density	Less power and/or range	Blend with diesel
	High bulk modulus	Advanced injection timing	Use common-rail fuel injection
	High surface tension	Larger fuel droplet affects combustion	Probably not a problem with low% biodiesel blends
	High iodine number	Lower fuel stability	Antioxidants

Lubricity Improvers

The implicit issue of low lubricity in F-T is mitigated by the fact that it is widely recognized and will be explicitly addressed in the next DFM MILSPEC (Williams and Chang 2008). Low lubricity is also a recognized problem with ultralow-sulfur diesel (ULSD) fuel. ULSD fuel is produced by robust hydrotreating, which removes all polar compounds, including the targeted sulfur (Figure 2), and can result in insufficient lubricity (Hughes et al. 2002, 2003; Lacey and Westbrook 1997). Whether the polar compounds are removed during processing (ULSD) or are absent because of the manufacturing practices (F-T fuel), the lubricity of the resulting fuel is impaired and needs to be augmented with lubricity improvers.

Although many polar compounds could improve fuel lubricity, lubricity improvers are typically oxygenated, as this improves emissions and ignition characteristics (Ribiero et al. 2007). In order of effectiveness, these compounds are carboxylic acids, alcohols, esters, aldehydes, ketones, and ethers (Figure 3). Being polar, these compounds will tend to hydrogen bond to the hydroxylated surface of metals and protect them from direct contact with other surfaces. In 5 of 6 tested fuels, phenolic compounds, which are mildly acidic aromatic alcohols, were found to be responsible for “native” fuel lubricity (Hughes et al. 2003). Lacey and Westbrook (1997) evaluated 18 commercial lubricity improvers, all of which were proprietary. The most effective products were added in the range of 100-200 ppm (mg/L).

**Figure 3. Generalized examples of oxygenated compounds that can be added to improve fuel lubricity.**

Although this report has focused on the unfavorable properties of biodiesel, when added to ULSD, it significantly improves the fuel’s lubricity (Anastopoulos et al. 2001a, 2001b;

Hughes et al. 2002; Knothe and Steidley 2005). Biodiesel, although mostly composed of fatty acid methyl esters, also contains traces of free fatty acids and mono-acyl glycerols that contribute greatly to the lubricity of biodiesel-ULSD blends (Knothe and Steidley 2005). Using biodiesel as a lubricity improver would only be prudent in cases where fuel is not stored in seawater-compensated tanks, because of the seawater-fuel stability problems demonstrated by Mushrush et al. (2005).

Fuel Stability

Fuel stability is general resistance to chemical changes in the fuel. Chemical changes in fuel can manifest as changes in color and physical properties, development of soluble or insoluble gums, particulates and sediments, coke and deposit formation, and changes in compatibility with other materials (Batts and Fathoni 1991). Some changes in fuel quality are manifested at low temperatures, while others are observed only at high temperatures. Gum, particulate, and sediment formation, which occur at low temperatures, can plug filters. Also occurring at low temperatures, changes that result in incompatibility with other materials, typically other fuels, can lead to production of solids and sludge, which results in fuel pump and filtration problems (Batts and Fathoni 1991). Coke and deposit formation, which occur at high temperature, fouls injectors and leads to rough engine running, poor emissions, and reduced power.

The stability of biodiesel fuel is largely a function of the unsaturated double bonds in fatty acid moieties of the feedstock, such as linolenic acid, linoleic acid and oleic acid (Dunn 2008; Knothe 2008; Paligová et al. 2008). These are equivalent to olefins in petroleum, and can be oxidized and/or polymerized to varnish or gums. Fuel oxidation can be limited by storage procedures, metal deactivators, and antioxidants. Since storage in an oxygen-free container is quite difficult, limiting oxidative reactions by using metal deactivators and antioxidants is discussed below. Both of these approaches are accepted in fuel MILSPECs.

Oxidative reactions in petroleum fuels are often catalyzed by metals, with copper a common culprit (Waynick 2001). Metal deactivators, as are cited in the JP-5 and JP-8 MILSPECs, work primarily by chelating metal cations, which prevents them from catalyzing oxidative reactions. Metal deactivators can have other protective properties, including surface passivation and mild Lewis/Brönsted base activity. Surface passivation physically separates a potentially catalytic surface from reactive substrates in the fuel. Base activity accepts protons, buffering and mitigating acid-catalyzed changes in the fuel (Waynick 2001).

Antioxidants protect other molecules from oxidation. They can preferentially react with oxygen or free radicals and/or they may stabilize free radicals and prevent them from further reactions. Antioxidants in fuel include various derivatives of phenol, either added or native to the fuel, including butylated hydroxytoluene (Balster et al. 2006; Hess et al. 2005), butylated hydroxyanisole (Hess et al. 2005), and pyrogallol (Paligová et al. 2008). These are shown in Figure 4, and Hess et al. (2005) show several other antioxidants. Hindered phenols, with groups that “block” the hydroxyl, are more effective than unhindered phenols (Batts and Fathoni 1991). Unhindered phenols react to form reactive hydroquinones that facilitate polymerization of deposits in fuel (Beaver et al. 2005).

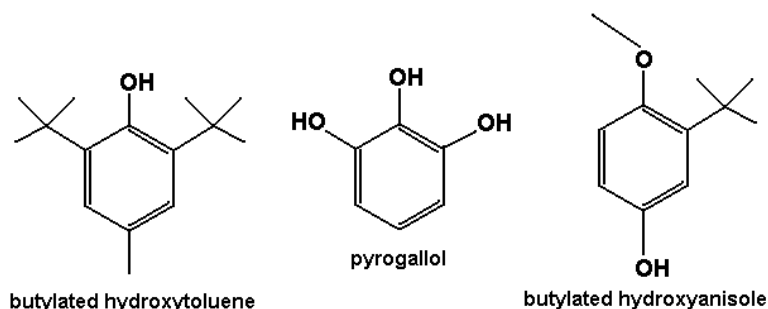


Figure 4. Examples of phenol derived fuel additives with antioxidant properties.

Conclusions

Blending alternative fuels with petroleum fuels will mitigate the issues of lower energy density and seal failures possible with alternative fuels. Use of a high-pressure, “common rail” fuel injection system would eliminate the issue of either higher or lower bulk modulus affecting fuel injection timing. Additives can improve the remaining limiting properties of F-T and biodiesel fuels. Lubricity additives can improve the low lubricity of F-T fuel. Antioxidant additives can improve the stability of biodiesel. The stability of biodiesel remains a serious issue in cases where fuel can be contaminated with water.

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