Naval Surface Warfare Center
Carderock Division
West Bethesda, MD 20817-5700

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Survivability, Structures, and Materials Department

Technical Report

A Survey of Alternate Fuels and Their Suitability for Use by the U.S. Navy

by

David M. Stamper, Jeffrey J. Fedderly,
Gilbert F. Lee, and Robert A. Brizzolara

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14. ABSTRACT
The purpose of this study was to determine the feasibility of Naval tactical and non-tactical use of alternative fuels as a way to reduce dependence on foreign oil and harmful air pollutants. The alternative fuels are divided into two classes: biofuels and manufactured fuels. The biofuels are the simple alcohols (methanol, ethanol, and butanol) that can be produced from biomass (various crops, grasses, trees, etc.) and biodiesel that is produced from various vegatable and animal triglycerides (oils and fats). The manufactured fuels are the Fischer-Tropsch (F T) and pyrolysis processes. These processes convert coal, natural gas, or biomass into liquid fuels that closely resemble petroleum fuels. The production methods and properties of these alternative fuels will be presented. This report also identifies S&T areas for future developments.

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EXECUTIVE SUMMARY

The Navy is looking to an increased use of alternative fuels as a means of reducing traditional petroleum fuel consumption. This report considers the suitability of liquid alternative fuels that can be used more-or-less as direct, commercially available replacements for existing traditional fuels or blended into existing fuels. These alternative fuels can be divided into two classes, biofuels and manufactured fuels. The main biofuels are the simple alcohols (methanol, ethanol, and butanol) that can be produced from biomass (various crops, grasses, trees, *etc.*) and biodiesel that is produced from various vegatable and animal triglycerides (oils and fats). Manufactured fuels utilize Fischer-Tropsch (F-T)/pyrolysis processes that convert coal, natural gas, or biomass into liquid fuels that closely resemble petroleum fuels.

This purpose of this study was to gather information on various alternative fuels for Navy use on ships, boats, air craft, and land vehicles. Specific goals of this report are to:

- Evaluate the suitability of alternative fuels for Navy use
- Assess the current technologies for production and the technical maturity.
- Identify gaps and issues that currently prevent more widespread use.
- Identify high-payoff areas for S&T investment.
- Make recommendation where appropriate for areas in which NSWCCD should be engaged in S&T.
- Formulate approaches of identified S&T areas.

The properties and suitability of methanol, ethanol, butanol, biodiesel, and F-T/pyrolysis fuels were investigated. Currently only ethanol and biodiesel are being used in appreciable quantities as alternative fuels. This use is in light-duty non-tactical vehicles such as cars, SUV’s, minivans, and pickup trucks that would otherwise use gasoline or standard diesel fuel. Vehicles of this type are being procured and run on alternative fuels in accordance to the Energy Policy Act of 1992 which mandates that 75 percent of such vehicles in Federal fleets use alternative fuels. Bio-fuels, including ethanol/gasoline blends such as E-85 and biodiesel and biodiesel/diesel blends, are the predominant alternative fuels.

The suitability of the various alternative fuels for use in tactical platforms, such as boats, ships, and aircraft was also investigated. These platforms generally run on either distillate (or diesel) fuel marine (DFM) or JP-5. The use of these fuels is currently mandated and the fuel properties are described in military specifications (MILSPECs). This makes the incorporation of alternative materials into the existing fuels significantly more difficult. This effort will evaluate the properties of alternative fuels to determine if they could be added to traditional fuels at appreciable levels and still meet or at least approach the MILSPEC values. An important fuel property specified in the MILSPECs is the flashpoint. The flashpoint of Navy fuels must be 60°C or higher, for safety reasons. Many alternative fuels have flash points below 60°C.

One of the most important properties of a fuel is its energy density (the maximum energy output upon combustion per unit weight or volume). This ultimately dictates the range of the vehicle. Of the bio-fuels, methanol and ethanol have energy densities that are significantly lower than the petroleum fuels. It is unlikely that they could be incorporated without significant sacrifice of performance. Biodiesel and butanol have intermediate energy densities of approximately 85 percent of the petroleum fuels. A 50/50 blend of either of these into DFM would result in a fuel with greater than 90 percent of the energy content of the existing fuel. Even at this high value, the Navy may not be willing to sacrifice even a few percent drop-off in performance. Biodiesel is currently being produced in large quantities as a transportation fuel and remains a viable alternative fuel candidate. Butanol has many attractive properties, but at this time is not being produced in appreciable quantities as a bio-fuel.

Fischer-Tropsch fuels can be tailored to mimic specific petroleum fuels. F-T fuels are attractive because they have energy densities that are comparable to petroleum fuels. Although these materials are not currently being produced in this country as a transportation fuel, the Navy is very interested in these types of materials due to their high energy content. However, using existing technology, they require significantly more energy to produce than they generate upon combustion and significant amounts of carbon dioxide are produced. This makes them less attractive from an environmental standpoint. The properties of F-T fuels and their status as an alternative fuel source are provided.

INTRODUCTION

The US Navy is looking to an increased use of alternative fuels as a means of reducing traditional petroleum fuel consumption. This report considers several liquid alternative fuels currently in use, or under consideration for use, in non-military applications. These fuels are evaluated for their suitability as direct (drop-in) replacements for, or as blends with, petroleum fuels used by the Navy. Both tactical and non-tactical uses are considered in this report.

Most liquid transportation fuels are refined from crude petroleum. Crude petroleum contains a large variety of hydrocarbon compounds, its composition varying depending on where it is found in the world. A combination of fractionation and reforming of crude petroleum is used to produce transportation fuels characterized largely on their boiling ranges. Once the lightest (less than 5 carbons) hydrocarbons are distilled off, gasoline, kerosene, diesel, and fuel oils (in order) are successively fractionated at higher temperatures. Heavier (higher boiling) fractions and residual petroleum can also be reformed (cracked) with hydrogen, heat, and pressure to be converted into lower boiling point fractions with higher demand, typically gasoline.

Gasoline, kerosene, and diesel fuels are widely used in transportation. Gasoline, with a lower flash point (-40°C), however, is not much used by the military as a tactical fuel as it is more dangerous to handle than the other fuels. Gasoline and gasoline blends are only used as non-tactical fuels, primarily for automobiles. Kerosene-based jet fuels are used in aircraft, and all aircraft useage should be considered tactical. Diesel fuel is used in heavy machinery, trucks, and ships, and may be considered both a tactical and non-tactical fuel.

The oil consumption by the Navy and Marine Corp is about 44Mbbl (million blue barrels of crude oil, 42 U.S. gallon per barrel) per year (Dimotakis, P., et al. 2006). A majority of the petroleum fuel is for by tactical vehicles and a smaller portion is for non-tactical vehicles (Turner, L. 2007). The amount of petroleum fuels used on Navy and Marine Corps installations for non-tactile vehicles is about 118,000,000 GGE (gasoline gallon equivalent) per year (U.S. Navy and Marine Corps AFV reports, 2006).

U.S. Navy Tactical Vehicle and Engine Types

Most aircraft carriers (CVN), and all attack (SSN) and ballistic missile (SSBN) submarines are powered by nuclear reactors driving steam turbines. Some conventionally powered ships use boilers that drive steam turbines, including one aircraft carrier (CV), ammunition ships (AE), most amphibious assault ships (LHA/LHD), amphibious command ships (LCC), and submarine tenders (AS). Several other classes are powered by diesel engines, including the dock landing ships (LSD), mine warfare ships (MCM/MHC), coastal patrol (PC), rigid hull inflatable boats (RHIB), and conventional landing craft (LCM/LCU). Gas turbine engines power the remaining Navy warships. These ships include some amphibious assault ships (LHD), amphibious transport dock ships (LPD), Perry-class frigates (FFG), Arleigh Burke-class destroyers (DDG), Ticonderoga-class cruisers (CG), and air cushion landing craft (LCAC) (U.S. Navy 2007). These are summarized in Table 1.

Cruisers, destroyers, and amphibious assault ships store their fuel in seawater-compensated tanks. As fuel is withdrawn, seawater is added to maintain full tanks. This is done for seakeeping purposes: to manage the buoyancy and stability of the ship. Fuel must, therefore, be compatible with seawater. Significant quantities of fuel must not dissolve into the seawater and *vice versa*. Similarly, the fuel should be minimally biodegradable, given a seawater "inoculum" of numerous microorganisms.

All manned Navy aircraft (fixed-wing and rotorcraft) are powered by gas turbine engines (Table 1) running on the kerosene-based jet fuel, JP-5 (described below). Land vehicles, used primarily by the Marines, are powered by diesel engines (Table 1). Newly fielded are diesel-engined motorcycles (Hayes Diversified Technologies 2007), designed explicitly to comply with the single-fuel concept (described below).

Both diesel and gas turbine engines are typically somewhat flexible with regard to acceptable fuels, being able to burn fuels from the kerosene (C_7 to C_{16}) through the diesel range (C_{10}-C_{22}). Kerosene fuels do present some problems for diesel engines, however, as they may not provide sufficient lubricity for the fuel injection system (Le Para 2005). Similarly, the use of diesel fuels in gas turbine engines can be limited to warmer environments due to fuel gelling. This is seldom a problem onboard ship, but is a critical issue for aircraft (at operational altitude). For this reason, aircraft are not flexible with regard to which fuel can be burned, even though turbine engines may be otherwise flexible. Boilers are more flexible than diesel or turbine engines, being able to burn practically any liquid fuel from JP-5 to IF-380 (described below).

Given a certain degree of flexibility in the fueling of diesel engines and less flexibility with regard to aircraft turbine engines, the overall DoD strategy is to have a single, kerosene-based battlefield fuel (the single fuel concept, SFC). Naval forces are moving in the direction of using JP-5 as the main fuel, while land-based forces are moving toward JP-8 as the main fuel. The SFC eliminates the possibility of mis-fueling and accomplishes certain logistical benefits (Le Pera 2005, Sermarini 2000, Giannini *et al.* 2002). There is sufficient capacity among petroleum refiners to satisfy all of the Navy's fuel needs with JP-5, albeit at a somewhat higher cost (Giannini *et al.* 2002, Sermarini 2000).

Table 1. Naval tactical vehicle types and corresponding engine and fuel types.

Tactical Vehicles	Engine Type	Fuel Type
Aircraft Carriers (CVN) Submarines (SSN, NAS, SSBN)	Steam Turbine	Uranium
Aircraft Carriers (CV) Ammunition Ships (AE) Amphibious Assualt Ships (LHA/LHD, most) Amphibious Command Ships (LCC) Submarine Tenders (AS)	Boiler	JP5[1] to IF380[2]
Dock Landing Ships (LSD) Mine Warfare Ships (MCM/MHC) Coastal Patrol Boats (PC) Rigid Hull Inflatable Boats (RHIB) Conventional Landing Craft (LCM/LCU) Marine Land Vehicles	Diesel (Compression Ignition)	DFM (F-76)[3]
Amphibious Assault Ships (LHA/LHD, few) Amphibious Dock Ships (LPD) Perry-Class Frigates (FFG) Arleigh Burke-Class Destroyers (DDG) Ticonderoga-Class Cruisers (GC) Air Cushion Landing Craft (LCLC)	Gas Turbine	Kerosene to Diesel (JP5 and/or DFM)
Aircraft	Gas Turbine	JP5 only

[1] JP5 is US Navy aviation kerosene (jet fuel)
[2] IF380 is a heavy fuel oil (intermediate fuel oil)
[3] DFM is distillate fuel marine, also known as F-76

There are three overriding issues in considering tactical alternative fuels. The first consideration is the DoD SFC. Any consideration of alternative fuels for DoD and/or Navy use must be consistent with the SFC, and have JP-8 and/or JP-5 as preferred targets. Any arguments for tactical use of alternative fuels in land or sea vehicles, while avoiding use in aircraft, would be difficult to make in light of the SFC. The second consideration, specific to the Navy, is the issue of seawater-compensated fuel tanks. In such tanks, as fuel is used, seawater is pumped into the tanks, as ballast, in order to maintain proper seakeeping. The density difference between and the immiscibility of the fuel and the seawater largely keep them separate, but some mixing does occur. Seawater-compensated fuel tanks are used in destroyers, cruisers, and amphibious assault vessels, in contrast to other vessels that have separate ballast tanks for maintaining seakeeping. Any tactical alternative fuels used by the Navy must behave suitably upon exposure to seawater. The third consideration of fuel stability in storage is also specific to the Navy. Fuels have to remain stable (sludge- and varnish-free) in storage, as specified in the MILSPECs for JP-5 and DFM.

Major U.S. Navy Tactical Fuels

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. This fuel is very similar to marine gas oil and No.2 diesel, but has tighter specifications, notably the cetane index and long term stability. The issue of stability is inherent in the DFM name, as a distillate fuel, not a reformed or cracked fuel, unlike marine gas oil and No.2 diesel. Petroleum reforming creates olefins (unsaturated hydrocarbons with carbon-carbon double bonds), which tend to crosslink over time, leading to sludge and varnish formation. DFM is the fuel normally used in internal combustion engines with compression ignition (diesel engines), but it can also be used as turbine fuel or for firing boilers.

The second main U.S. Navy fuel is aviation jet fuel (JP-5). This is a kerosene based, lower-boiling fraction than diesel, with specifications for a significantly higher flash point (60°C) than other jet fuels (eg. JP-8). The use of JP-5 is peculiar to U.S. Navy for aviation purposes, but can also be used in diesel engines and to fire boilers. The basic physical characteristics of JP-5 and DFM are shown in Table 2, along with the alternative fuels discussed in this report.

Both JP-5 and DFM have a min 60°C flash point for safety reasons. Most diesel fuels would inherently meet the 60°C flash point. “Typical” jet fuels, like JP-8, have a much lower flash point (approximately 48°C) and pose additional risk for shipboard use. Shipboard safety considers both the standpoint of reduced fire risk and reduced crew exposure to vapors, both of which are critical in confined shipboard spaces (Global Security 2007b). From a flammability standpoint, Affens (1976) suggests a useful safety margin of storage and use ranging 3-11°C below the fuel’s measured flash point, and others (Global Security 2007a) state that the conditions under which the fuel is used should be at least 10°C cooler than the flash point of the fuel.

The first “JP-5” MILSPEC (MIL-F-7914) dates to 1952. Prior to this point, JP-4 was the primary aviation fuel. In 1948, the United Kingdom developed a specification for carrier-borne aviation fuel with a 65°C flash point (similar to the diesel fuel already carried onboard), but this high flash point meant that production of appropriate jet fuel was limited and ended up being problematic. Probably motivated by the British experience, the U.S. Navy issued MIL-F-7914 with a more easily attainable (30-60 percent higher yield) 60°C flash point (Mearns 1991). The current JP-5 MILSPEC is the MIL-F-5624 series.

The 60°C flash point is a compromise that is 1. high enough to provide a substantial margin of safety relative to “typical” kerosene-based fuel (JP-8: approximately 48°C flash point), 2. low enough not to adversely affect other important properties like viscosity and freezing point, and 3. attainable at a reasonable yield and cost (Affens 1976). The 60°C minimum flash point requirement has actually been revisited several times over the last 50 years in response to fuel costs and availability, but never overturned (Mearns 1991).

Some safety-related comparisons between JP-5 and JP-8 have been investigated by Wells *et al.* (1998). In spark ignition testing at 71°C, a JP-5 spill is ignitable at less than 5 mm height while a JP-8 spill is ignitable at 30 mm. At 60°C, these heights are reduced to ≤1 mm and 20 mm for JP-5 and JP-8, respectively. The maximum flame spread rate of JP-5 is both lower than JP-8 (4 feet per second *vs.* 5 fps) and remains low (less than 0.3 fps) at 65°C, whereas flaming JP-8 is already spreading at approximately 4 fps. These experiments vividly demonstrate that JP-5 is both harder to ignite than JP-8 and, even when they are ignited, fires from JP-5 spread somewhat more slowly than those from JP-8.

Table 2. Basic physical characteristics of the major U.S. Navy tactical fuels JP-5 and diesel (DFM), along with the biofuels and F-T fuel.

Physical Characteristic	**JP-5**	**DFM**	**Methanol**	**Ethanol**	**Butanol**	**Biodiesel**	**F-T Fuel**
Molecular Weight and/or Chemical Formula	C_8-C_{16} [A]	C_{10}-C_{22} [A]	32.0 CH_3OH	46.0 CH_3CH_2OH	74.1 $CH_3(CH_2)_3OH$	$C_{16} – C_{18}$ [I]	Made to Order
Density (kg/L)	0.79-0.85 [H]	<0.876 [D]	0.79 [B]	0.79 [B]	0.81	0.88 [J]	Similar to petroleum
Energy Density (MJ/kg)	42.6 (min) [C]	45-50 [D,E]	23 [E]	30 [E]	37	38[J]	43, est.
Energy Density (MJ/L, nominal)	35.3	40.4	18.2	23.7	30.0	32.9 [J]	36, est.
Flash Point (°C, open cup)	≥ 60 [C]	> 60 [D]	11[G]	9 [G]	27	130 [K]	Similar to petroleum
Melting Point (°C)	-46 [C]	≤ -1 [D] (cloud point)	-94 [B], -98 [G]	-117 [B], -130 [G]	-90	-3 - 19 [L]	Similar to petroleum
Boiling Point (°C)	205-300 [C]	200-385 [D]	65.0 [B,G]	78.5 [B,G]	118	360 [K]	Made to Order
Viscosity (cSt 20°C)	8.5 (max) [C]	1.7-4.3 @ 40°C [D]	0.74 [F]	1.5 [F]	3@25°C	1.9 – 6.0 [I]	Similar to petroleum
Acidity	<0.1 mg KOH/g [C]	<0.3 mg KOH/g [D]	$pK_a = 15.5$ [D]	$pK_a = 15.9$ [D]	$pK_a = 16.1$	0.5 mg/KOH/g [K]	Similar to petroleum

[A] www.chevron.com/products/prodserv/fuels

[B] Handbook of Chemistry and Physics

[C] MIL-DTL-5624U: Mil-spec for JP-5.

[D] MIL-DTL-16884L: Mil-spec for DFM

[E] xtronics.com/reference/energy_density.htm

[F] www.engineeringtoolbox.com/kinematic-viscosity-d_397.html

[G] MSDSs from Sigma Aldrich (St. Louis, MO)

[H] www.atsdr.cdc.gov/toxprofiles/tp121-c3.pdf

[I] National Biodiesel Board, 2007, Weight&Formula.pdf

[J] National Biodiesel Board, 2007, BTU_Content_final.pdf

[K] ASTM D6751-06B

[L] Biodiesel Handeling and Use Guidelines, Department of Energy, 2006

Minor U.S. Navy Tactical Fuels

In addition to the major Navy fuels, minor fuels in use by the U.S. Navy are marine gas oil (MGO) and the intermediate fuel oils (IFO 180 and IFO 380). These minor fuels are not stable over the long-term and must be used before sludges are formed in the tanks. MGO is synonymous with No.2 fuel oil and similar to DFM, except that it contains both petroleum distillate and reformate. MGO can be used in diesel engines and to fire boilers. IFO-180 and IFO-380 are defined by their viscosity (180 or 380 cSt @ 50°C) and are composed of mixtures of petroleum distillate and reformate (MGO or equivalent) and residual petroleum fractions. The IFOs are used for firing boilers and are not suitable for use in turbine or diesel engines.

U.S. Navy Non-Tactical Vehicles and Fuels

U.S. Navy and Marine Corps facilities have an ongoing program to encourage the use of alternative fuel vehicles and domestic produced fuel. Principal Deputy Assistant Secretary (Installation and Environment) Wayne Arny (National Biodiesel Board, 2005) has issued a memorandum that establishes a policy for all U.S. Navy and Marine non-tactical diesel vehicles to operate on a blend of 20 percent biodiesel fuel (B20) no later than June 2005. The Energy Policy Act of 1992 (EPAct) requires that 75 percent of all covered light-duty vehicles acquired for Federal fleets in FY 1999 and beyond must be alternative fuel vehicles, except for certain emergency, law enforcement, and national defense vehicles are exempted. The EPAct has also set a goal of using alternative fuels to displace at least 30 percent of the projected consumption of petroleum fuel in the United States annually by the year 2010.

The types of alternative fuel vehicles (U.S. Navy and Marine Corps AFV reports, 2006) includes sedans, pickup trucks, minivans, and light and medium duty trucks, used on Navy and Marine Corps facilities are listed in Table 3. The quantities of biofuels and petroleum diesel and gasoline used are listed in Table 4 for 2006. The quantity of biofuels is expected to increase as the number of alternative fuels vehicles to be purchase for 2007 is also increasing.

Table 3. FY 2006 Navy and Marine Corps non-tactical vehicles and types of fuels (gasoline, petroleum diesel, biodiesel, and alternative fuel vehicles)

Fleet of Vehicles (Exemptions)	Gasoline, Petroleum Diesel
Sedan	CNG (Bi-Fuel), E-85 (Flex-Fuel)
Pickup 4x2	CNG (Bi-Fuel), E-85 (Flex-Fuel), LPG (Bi-Fuel)
SUV 4x2	E-85 (Flex-Fuel), CNG (Bi-Fuel)
Minivan 4x2	CNG (Bi-Fuel), CNG (Dedicated), E-85 (Flex-Fuel)
Bus	CNG (Bi-Fuel), CNG (Dedicated), LNG (Bi-Fuel)
Van MD (Passenger & Cargo)	CNG (Bi-Fuel), CNG (Dedicated)
MD 8,501-16,000 GVWR	CNG (Bi-Fuel), CNG (Dedicated), E-85 (Flex-Fuel)
HD 16,001 + GVWR	CNG (Bi-Fuel), CNG (Dedicated)

Bi-Fuel/Flex Fuel – Capable of using gasoline, petroleum diesel, and biodiesel.
CNG – Compressed Natural Gas
E85 – 85 percent ethanol and 15 percent petroleum (gasoline)
GVWR – Gross Vehicle Weight Rating
HD – Heavy Duty
LNG – Liquefied Natural Gas
LPG – Liquefied Petroleum Gas (Propane)
MD – Medium Duty

Table 4. FY 2006 Navy and Marine Corps fuel consumption for non-tactical vehicles

Fuel Use	**Marine Corps**	**Navy**
Alternative Fuel	**GGE**	
B100	315,343	
B20		484,865
CNG	238,542	79,870
E85	74,359	44,308
Electricity	0	0
LNG	0	0
LPG	1,833	0
Propane	0	6
Total Alternative Fuel Use	314,734	609,049
Petroleum	**GGE**	
Diesel	1,585,201	1,155,200
Gasoline	5,937,358	9,787,513
Total Petroleum	7,522,559	10,942,713

CNG – Compressed Natural Gas
E-85 – 85 percent ethanol and 15 percent petroleum (gasoline)
GGE – A gasoline gallon equivalent (GGE) is the amount of fuel required to equal the energy content of one liquid gallon of gasoline. A GGE is a way of comparing equivalent volumes of fuel based on the energy content in British thermal units (Btu).
LNG – Liquefied Natural Gas
LPG – Liquefied Petroleum Gas (Propane)

ALTERNATIVE LIQUID FUELS

In this document we describe several alternative fuels currently in use or under consideration for use in non-military applications, and evaluate their suitability for Naval use, production, energy balance, costs, technological gaps, and research opportunities. Low-volume, specialty fuels are beyond the scope of this report, even though they might otherwise have Navy uses. This report focuses on methanol, ethanol, butanol, and biodiesel, as well as the fuels derived from pyrolysis and the Fischer-Tropsch process (the main topics of a workshop on alternative fuels sponsored by the Office of Naval Research in June, 2007).

Methanol

Sources and Production

Methanol (CH_3OH) is the simplest alcohol, containing a single carbon atom. Although historically produced as a distillation product of wood, nearly all methanol is currently produced by combining methane (natural gas), steam, and/or oxygen to produce a mixture of carbon monoxide (CO) and hydrogen (H_2), called syngas (Roan *et al.* 2004, Spath and Dayton 2003).

Syngas production:

$$CH_4 + H_2O(g) \rightarrow CO + 3H_2 \qquad \Delta h = +206.16 \text{ kJ/mol } CH_4$$

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2H_2 \qquad \Delta h = -36 \text{ kJ/mol } CH_4$$

The syngas is catalytically reformed into methanol, and may involve adding CO_2 to take advantage of any stoichiometric excess of hydrogen. Syngas formation from methane is enhanced by high temperature and moderate pressure (Spath and Dayton 2003), so some (≤ 25 percent) of the natural gas feedstock is burned to provide the balance of energy to fuel the production of steam and any remaining endothermic debt (increase the temperature), again depending on the hydrogen concentration of the syngas. Typically, syngas is reformed into methanol over catalysts, assisted by cooling and at higher pressure, as described below.

Methanol reforming:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta h = -90.64 \text{ kJ/mol}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta h = -49.67 \text{ kJ/mol}$$

The cost to produce methanol depends largely on the cost of natural gas according to:

$$MeOH_{(\$/gal)} = 0.0813 * NG_{(\$/TCF)} + 0.0292$$

where MeOH is the cost of methanol per gallon and NG is the cost of natural gas per thousand cubic feet (TCF). For example, with natural gas at $6 per TCF, the cost to produce methanol is

$0.52 per gallon (Roan *et al.* 2004). Spot prices (not including delivery) for bulk methanol ranged from $0.70-0.80 per gallon in 2004 (Table 5).

Direct use of natural gas as a transportation fuel is possible, with buses, commercial vehicles, and even non-tactical military vehicles (Table 3) modified to use natural gas. Nonetheless, given the difficulty in transporting natural gas and/or compressing it, both of which consume a large amount of energy and require specialized equipment, natural gas is not a widely suitable transportation fuel and is not a suitable fuel for U.S. Navy tactical use.

Energy and Carbon Balance

For every unit of fossil energy that goes into methanol production, less than one unit of energy is available in the methanol, because methanol is produced almost exclusively from fossil fuel (largely natural gas). Because biomass is produced with solar energy (in large part), to the extent that biomass can be used to produce syngas, the energy balance would increase.

Given heats of combustion of 56 kJ/g for methane and 23 kJ/g methanol (Table 2), the stoichiometry of converting methane to methanol (16 g methane ≈ 24 g methanol), and estimating 20 percent of the natural gas feedstock used to drive the process, the energy ratio (energy out/energy in) of methanol production from natural gas is approximately 0.5 (Table 5). By retaining only 50 percent of the original chemical energy of natural gas, this process is economically favorable only where the local abundance of natural gas is greater than the combined local natural gas and electrical demands. Methane reformation into methanol is particularly sensible for remote and "stranded" sources of natural gas, given that liquid methanol is much easier to transport than natural gas.

Although methanol produced from natural gas dominates the world market, the domestic production of methanol from coal will likely become more important over the next several years or decades, as native natural gas supplies dwindle and prices increase. The U.S. is already a net importer of natural gas (approximately 18 percent of needs) and this will increase over time (Roan *et al.* 2004). Our growing dependence on the foreign supply of natural gas will increase U.S. strategic difficulties, much as with our petroleum usage. Coal, as an abundant native energy source and capable of being converted into transportation fuel, is a strategically important resource for the U.S. The burning of coal produces the most CO_2 of any fuel, however, which is a concern because CO_2 is implicated as a greenhouse gas.

Electrical production involving coal gasification is approaching maturity using the combined cycle. In the combined cycle, coal can be gasified with steam and oxygen (not air) at high temperature, producing syngas that is burned in the primary turbine. The remaining (residual) heat is subsequently used to produce steam for a steam turbine. Both the primary and the steam turbines turn generators to make electricity, resulting in higher thermal efficiency (approximately 50 percent *vs.* 25-35 percent) compared to directly burning the coal to produce steam (Roan *et al.* 2004).

Table 5. Economic and practical considerations for alternative fuels considered in this report

	Methanol	**Ethanol**	**Butanol**	**Biodiesel**	**F-T Fuel**
Energy Ratio [*]	~0.5 from natural gas	From 0.7-1.3 (corn)[1,2] ~1.8 (cellulosic)[2]	Assume ethanol values or somewhat greater	0.79[5] – 2.51[6]	0.4-0.5 from fossil sources
Coproducts in Energy Ratio	None from fossil sources	Corn feed, meal, and oil and distillers grains	Corn feed, meal, and oil and distillers grains	Soybean meal, glycerine	None from fossil sources
Bulk Cost from Source ($/gal.)	$0.70-0.80 from natural gas, 2004[3]	$1.04 from corn $0.91 from cellulose $0.30-0.60 optimistically[2]	$1.20 from corn $0.85 from whey	$2.49[7] soybean	Est. $1.00/gal
Subsidies ($/gal.)	None from fossil sources	$0.51 federal (2005) $0.20± some states	Should be the same as ethanol	$1.47[7]	None from fossil sources
Distribution Cost [#] ($/gal equivalent), diesel = $0.19/gal	$0.42 + cost for infrastructure	$0.32	$0.26	$0.23	$0.21
Cost per MJ (¢), including subsidies	1.8¢ @ $0.80/gal.	0.73¢ from corn	0.66¢ from corn	1.0¢ from soybean	0.89¢ @ $1.00/gal
Infrastructure Issues	Corrosive Similar to ethanol	Water contamination Higher volatile emissions	None	None	None
Scale of Production (gal/yr/plant)	113 million	Generally >1 million Ave = 38 million	Research quantities	400 thousand to 50 million	52 million gal/yr[4]

[*] Energy Ratio: Energy of the Fuel / Energy to Produce the Fuel (greater than 1.0, implies a net enrgy gain)

[#] Distribution cost: Estimates the cost to distribute alternative fuels, normalized to the higher energy density of diesel fuel.

[1] Pimentel, D. 2003.

[2] www.eia.doe.gov/oiaf/analysispaper/biomass.html

[3] www.methanol.org

[4] www.sasol.com/sasol_internet/downloads/sasolfacts_2007_1180093894888.pdf

[5] Pimentel, D. and Patzel T.W., 2005.

[6] Ahmed, I., Decker, J., and Morris, D., 1994.

[7] http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/index.html.

Another benefit of combined cycle coal combustion is the higher concentration of CO_2 in the effluent gas, making CO_2 sequestration less expensive than with direct-fired coal; thus promises of “clean coal”. This is primarily because the low partial pressure of CO_2 in the flue gas from a direct-fired coal plant requires a chemical absorption process rather than the physical absorption possible with a combined cycle plant. For chemical absorption processes, the regeneration requirements are much more energy intensive (Woods *et al.* 2007). With CO_2 sequestration, the overall thermal efficiency would be approximately 43 percent (Martinez-Frias *et al.* 2003). To put it into perspective, electricity from clean coal technology (using CO_2 sequestration) should be approximately 50 percent more expensive (Woods *et al.* 2007).

A coal gasification electrical plant combined with syngas reformation to methanol could produce methanol for approximately $0.50 per gallon, which is no more expensive than from natural gas. The up-front capital costs required are much higher (Roan *et al.* 2004), however, making investments in this technology perhaps less attractive.

Historically, methanol was also produced by pyrolysis of woody material to make syngas, a process equivalent to that described for coal, with catalytic reformation into methanol. Methanol production from natural gas both has a higher yield and is less complicated (*i.e.* less capital investment) than from woody material or coal, explaining why most methanol is produced this way (Spath and Dayton 2003, Hokanson and Rowell 1977). Although methanol produced from natural gas is less expensive, strategic and environmental considerations may be changing the raw economic calculations of methanol production to favor the production of methanol from biomass. Production of methanol from biomass has the same strategic benefits as methanol production from coal (greater domestic transportation fuel production), but with much greater environmental benefits. The energy balance of methanol from biomass should be greater than 1.0, perhaps greatly so, depending on how much fossil energy is used in producing, harvesting, transporting, and transforming the biomass.

A study looking into methanol production from pulp mill effluent determined that producing methanol would be cost effective relative to typical on-site treatment (burning the pyrolysis gas to produce electricity). It is important to note that the Swedish CO_2 tax accounted for approximately 25 percent of the calculated value of methanol produced in this manner (Ekbom *et al.* 2003). The process is similar to methanol from coal gasification, with a portion of the pulp waste-derived syngas being diverted to produce methanol, rather than being burned for combined cycle electrical generation. Current federal tax credits (approximately $0.50/gal) in the U.S. for biofuels may favor a similar approach. The same report (Ekbom *et al.* 2003) calculates that methanol production from pulp mill effluent in the United States, alone, could equal the total worldwide production of methanol from fossil sources (30 million tonnes).

Methanol as Fuel

Methanol has been blended with gasoline and marketed in California from the mid 1980s through the late 1990s. Ford, Chrysler, and GM produced more than 15,000 flexible fuel vehicles for use with 85 percent methanol plus gasoline (M85), with a significant (approximately 40 percent) mileage penalty because of the lower energy density of methanol. Infrastructure issues with methanol meant accommodating the corrosivity and solvent characteristics of methanol (Table 5). For example, M85 capable vehicles had stainless steel fuel tanks and fuel lines, and methanol-compatible elastomer seals. An additional complication is that low concentration methanol blends (e.g. 10-20 percent methanol) tend to phase-separate, explaining why M85 was used. M85 is no longer marketed, limiting the possibile non-tactical use of methanol by the Navy.

Although methanol has approximately 50 percent the energy density of gasoline (Figure 1 and Table 2), purpose-built internal combustion engines can take advantage of the higher octane rating of methanol and run at a higher compression ratio. The gains in efficiency made possible by higher compression and other modifications can substantially offset or even neutralize the lower volumetric energy content (MPG) of methanol relative to gasoline (Brusstar *et al.* 2002). The internal combustion engine technology for using methanol in this fashion is mature, and Indy cars and some other race cars have been using 100 percent methanol (M100) for decades, up until 2007 when the Indy Car Series switched to 100 percent ethanol. Infrastructure for methanol use could be adapted from current gasoline infrastructure, as was done in California for M85. Regular commercial engines designed for methanol-gasoline blends cannot, however, exploit the higher combustion efficiency possible with a high compression ratio engine burning neat methanol.

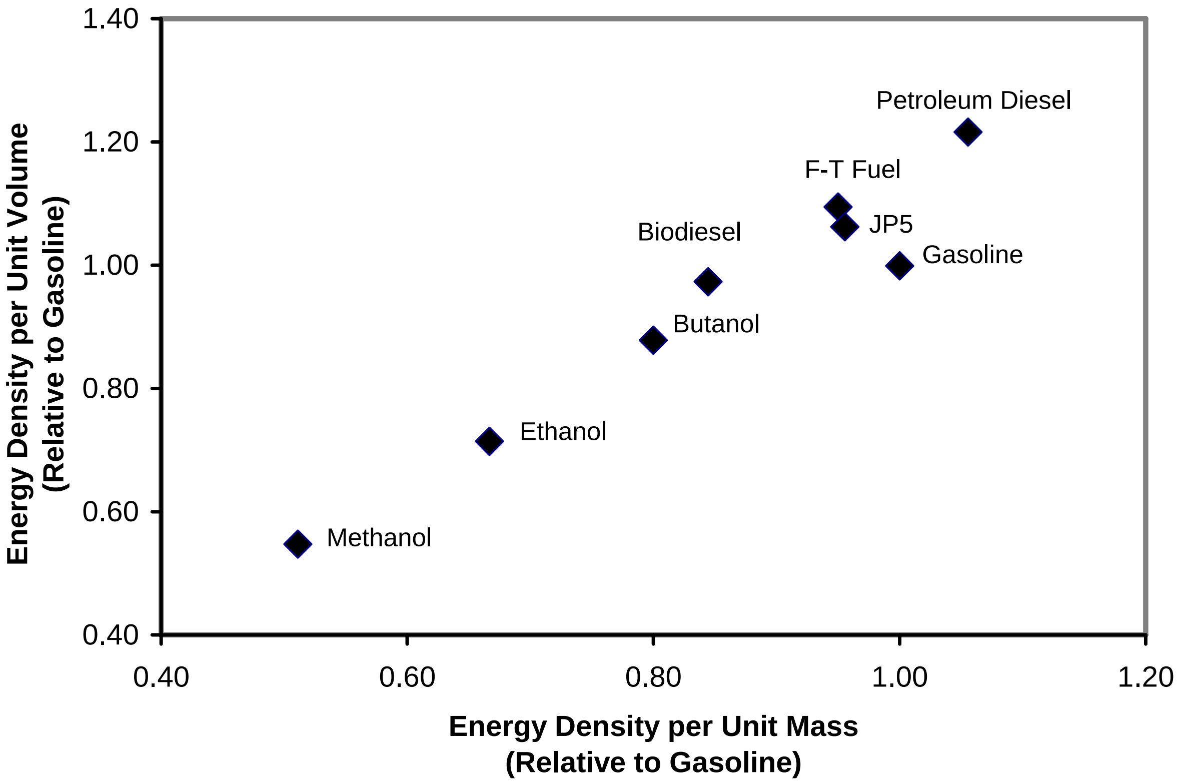


Figure 1. Relative energy densities (per mass and volume) of the several alternative fuels under consideration in this report, along with gasoline, DFM, and JP-5. Energy density values have been standardized with gasoline = 1.0.

Fuel cells can be approximately twice as efficient as internal combustion engines under some conditions, although efficiency decreases under high load, the opposite of most internal combustion engines. Use of methanol directly in low temperature fuel cells is largely limited to low-power applications, but some high temperature fuel cells can use methanol, essentially as a hydrogen carrier (Roan *et al.* 2004). This is currently limited to larger vehicles like buses, however. Although the DoD and Navy are interested in fuel cells, the goal is a high temperature fuel cell to run on jet fuel. Methanol fuel cells would probably only serve a small (niche) role, used in powering portable electronic equipment such as radios (Smith 2007).

A number of issues combine to make a methanol-diesel blend problematic. Most importantly, low concentrations of methanol in diesel are not feasible because of phase-separation. High concentrations of methanol in diesel are not acceptable, however, because the low cetane index of methanol would make ignition difficult (or impossible). Given that methanol has approximately 50 percent the energy density of petroleum diesel fuel, blending methanol into diesel would hinder performance and mileage. Additionally, any diesel vehicles would have to be modified to cope with the corrosivity and the lower lubricity of methanol. These issues may explain why little information about methanol-diesel blends could be found. Methanol-diesel may not be possible even for general or non-tactical use, let alone acceptable for DoD or Navy tactical uses.

The last conceivable DoD use of methanol would be as a turbine fuel. Turbines are generally fairly flexible with regard to fuels, and methanol can be used to fire turbines. Benefits include much lower sulfur and nitrogen oxides (NO_x) emissions, and reduced maintenance for cleaning. Modifications to accommodate the low flash point, low lubricity, and low energy density of methanol relative to petroleum-based fuels are required, however (General Electric 2001). Although turbine engines can run with methanol, the low flash point (11°C) of methanol and the requirement that the fuel be compatible with seawater compensated fuel storage makes it completely unacceptable as a turbine fuel for Navy use. Methanol is completely miscible with seawater. Moreover, the low energy density (23 *vs.* 43 MJ/kg for JP-5, Table 2) of methanol would approximately double the fuel logistics issues for the Navy, even if the safety and storage concerns could be ignored. Thus, methanol and methanol-blended fuels are completely inappropriate as Navy tactical fuels.

Economic and Technological Gaps

Given that natural gas reformation and coal gasification are technologies that have been in use since the 1920’s, this is essentially a mature, large-scale technology. A large variety of catalysts is well-characterized and can be chosen depending on feedstock, cost, and product purity (Spath and Dayton 2003). The driving force behind increased fuel methanol production will be the rising price of petroleum and the anticipation of higher petroleum prices, though government initiatives could help. Higher fuel prices will make the exploitation of stranded natural gas, combined coal gasification, and biomass such as pulp mill effluent and lignocellulose more economically favorable.

Any biomass can be gasified to produce methanol, so one could envision a plant 1. producing ethanol from cellulose and starch by fermentation, 2. producing biodiesel from vegetable oil and methanol by transesterification, and 3. gasifying the remaining lignin and any carbonaceous (waste biomass, coal, natural gas) products into syngas for methanol and electrical power. The methanol could be used on-site for the biodiesel production, with ethanol and any remaining methanol to be blended with gasoline or used in purpose-built alcohol-burning engines (Figure 2).

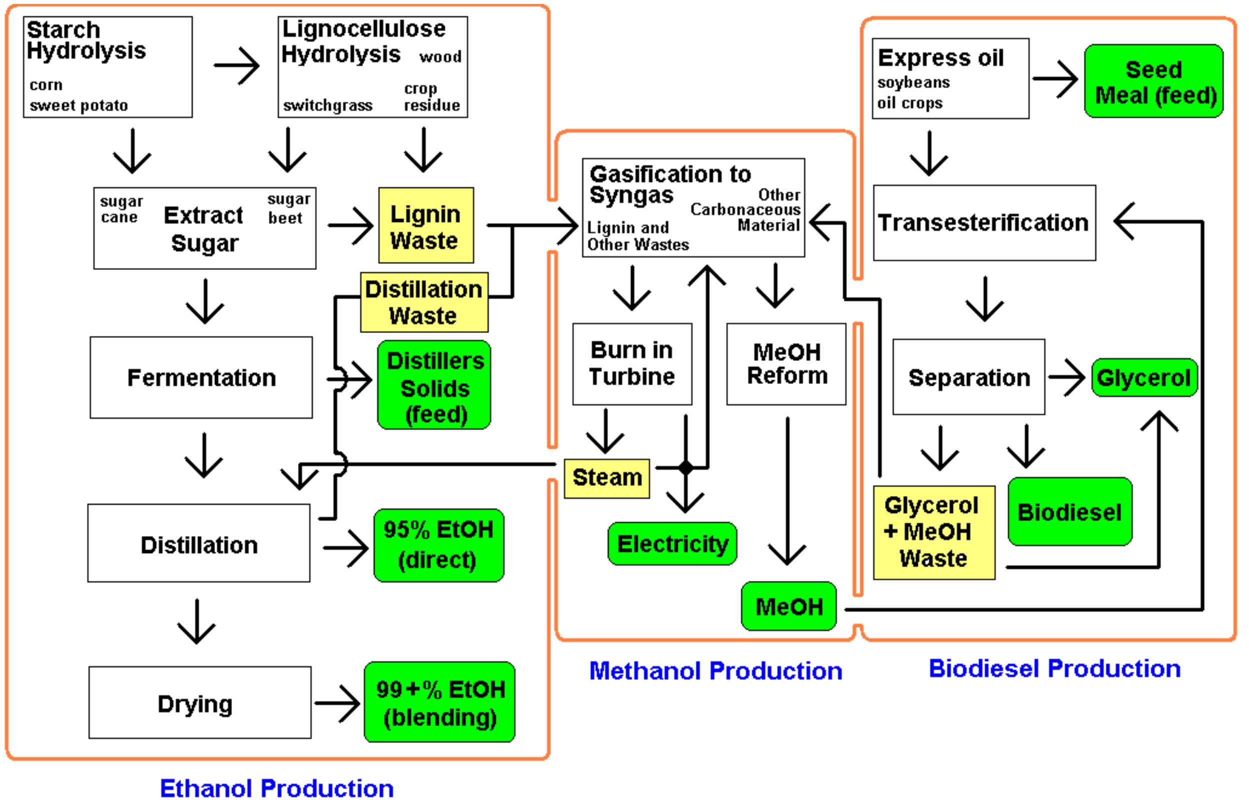


Figure 2. Schematic of a model biorefinery that integrates ethanol, methanol, and biodiesel production. Indicated are major processes (plain boxes), intermediates (yellow boxes) and products (green boxes). Ethanol production could be from any number of materials, as shown. Waste organic material from ethanol production is gasified, along with other organic material, to produce methanol, steam, and electricity. Combined cycle steam from the burning of syngas is used to distill ethanol, produce electricity, and/or recycled into syngas, as necessary. Methanol from syngas reforming is both a product and an intermediate for biodiesel and glycerol production. Total products from such an integrated facility would include ethanol, methanol, and biodiesel liquid fuels, and electricity, glycerol, and animal feed.

Potential for Carderock Division in Methanol Research, Development, Testing, and Evaluation (RDT&E)

Methanol production is a large-scale (100 million gallons/yr/plant, Table 5) and mature technology. Moreover, methanol is not useful as an alternative transportation fuel for the U.S. Navy for the reasons discussed above. Methanol as an alternative fuel for civilian transportation could have indirect benefits for the DoD, however. If alternative fuels are able to relieve some market pressure and improve the U.S. strategic position on energy, the DoD could benefit indirectly. In spite of any indirect benefits to the Navy from increased use of methanol as a transportation fuel, there is little justification for the Carderock Division to be involved in any methanol RDT&E.

Ethanol

Sources and Production

Ethanol (CH_3CH_2OH) has been produced in the form of alcoholic beverages for millennia. The use of ethanol as motor fuel dates back to the invention of the internal combustion engine by Nikolaus Otto (EIA 2007). The switch to petroleum-derived fuels came about because abundant sources of petroleum were discovered in the early 20th century.

Ethanol is very similar to methanol and, like methanol, can be made from fossil energy sources. Most ethanol (greater than 90 percent), however, is made by the yeast, *Saccharomyces cerevisiae*, through anaerobic fermentation of sugars according the reaction:

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2CH_3CH_2OH$$

S. cerevisiae can only ferment 6-carbon sugars, principally glucose and fructose, although it can also break down some di-saccharides (sucrose and maltose) into mono-saccharides. Some strains of *S. cerevisiae* are highly tolerant of ethanol, yielding greater than 15 percent ethanol. Many bacteria can also produce ethanol, but few strains approach 5 percent ethanol tolerance, even if they otherwise produce ethanol efficiently.

A higher final concentration of ethanol at the end of fermentation affords a lower cost for concentrating the ethanol into a useful product. Ethanol is typically concentrated by distillation to 95-96 percent ethanol. Residual water can be removed by several methods to yield pure ethanol. The sugar substrates for ethanol production are derived largely from three kinds of crops: 1. sugar-producing crops, 2. starch-producing crops, and 3. cellulose-producing crops (Figure 2, left box). The economic justifications for using sugar, starch, or cellulosic crops all hinge on the combined costs of the feed stock, the consumables (enzymes and energy), and the capital costs (facilities).

Ethanol production from sugar-producing crops is less capital- and consumables-intensive, as simple sugars (mono-saccharides) and di-saccharides are easy to extract, process, and ferment. Sugar cane, sugar beets, and fruits are examples of sugar-producing crops that are used in ethanol production. The sugars are extracted by mechanically disrupting the material and extracting with water. This is diluted, the pH and ionic strength are adjusted, nutrients are added, and the solution is pasteurized or sterilized by heating. Once cooled, the yeast cultures are added. Ethanolic fermentation is an anaerobic process, so no aeration is required. The yeast ferments sugars into ethanol and CO_2, with 90 percent of the energy content of the sugars remaining in the ethanol. Brazil produces most of its ethanol this way, using sugar cane as the feedstock.

Producing ethanol from starches is more complex, because starch is an insoluble, branched α-glucose polymer. After mechanical disruption, starch is broken down into mono- and di-saccharides. First, the starch is liquefied at pH 5.8-6.5 for 5 min. at 105-110°C, then partially hydrolyzed, using a heat stable enzyme (α-amylase) from the bacterium *Bacillus stearothermophilus*, at 95°C for 2-3 hrs. This liquefied starch is acidified to pH 4.2-5.0 and the temperature lowered to 55-60°C. Glucose (95-96 percent) syrups are produced with by the action of bacterial and fungal enzymes, namely pullulanase and glycoamylase, on the partially hydrolyzed starch. Maltose (80-85 percent) syrups are produced by pullulanase and β-amylase on partially hydrolyzed starch (Vielle and Zeikus 2001). Glucose and/or maltose sugar syrups are cooled further, and the process proceeds as described for simple sugars.

The extra heating and cooling steps, growing up bacterial and fungal cultures, and extracting and purifying enzymes all make the processing of starchy crops for ethanol more expensive than for sugar crops. The multiple pH adjustments, by increasing the salt concentration, also result in some inhibition of subsequent fermentation (*i.e.* additional cost). Most ethanol production in the U.S. follows this process, using corn as the starchy feed stock.

Use of cellulosic crops as the feedstock for ethanolic fermentation is a developing technology at the early stage of commercialization. The use of cellulose (actually lignocellulose) is appealing since crops such as switch grass and agricultural wastes such as corn stover and wood are the most abundant and inexpensive possible biomass feed stocks. Lignocellulose, responsible for the structural rigidity of plants, is a complex polymer composed of lignin, cellulose, and hemicellulose polymers that are physically and chemically interconnected. Lignin, a polymer composed largely of a variety of substituted phenols, composes 5-30 percent of the dry weight of plants. Lignin encapsulates and covalently bonds to hemicellulose and cellulose, physically protecting cellulose from enzymatic attack (Larsson *et al.* 2001). Cellulose, a β-glucose homopolymer, makes up 35-50 percent of plant dry weight (Lynd *et al.* 2002). Although a glucose polymer similar to starch, the β-bonding changes the structure, and cellulose is much more crystalline and difficult to enzymatically hydrolyze. Hemicellulose is a variable, amorphous, mixed polymer of 5- and 6-carbon sugars, with a 5-carbon sugar (xylose) being predominant. Hemicellulose comprises 20-35 percent of plant dry weight (Lynd *et al.*, 2002).

Production of ethanol from cellulosic materials involves first disrupting the physical structure of lignocellulose with solvents, heat, and/or reactive chemicals (Table 5). Each approach is designed to separate the protective lignin, which cannot be fermented to ethanol, from the cellulose and hemicellulose, which can be broken down into fermentable sugars. A major issue with using lignocellulosic materials is that xylose and other 5-carbon sugars from hemicellulose normally cannot be fermented by *S. cerevisiae*, potentially limiting the process efficiency.

Even when the physical structure of lignocellulose is disrupted, the cellulose is typically not extensively altered (Table 6). Cellulose, being highly crystalline, is a very difficult substrate for enzymes, making for longer reaction times. As a large polymer, cellulose cannot be transported into the cell, and multiple extracellular fungal cellulases (enzymes) are required to break it down. These enzymes include endoglucanases, exoglucanases, and β-glucosidases. Endoglucanases break down the internal bonds of amorphous (non-crystalline) cellulose to shorter cellulose polymers that can then be acted on by exoglucanases. Exoglucanases break down the terminal ends of crystalline cellulose to the oligomers cellobiose and cellotriose. β-glucosidases act on cellobiose and cellotriose, breaking them down into glucose, and are the least stable and most expensive of cellulases (Lynd *et al.* 2002).

Table 6. Effects of pretreatments on lignocellulose. After Lynd *et al.* 2002.

Process	**Effects on Lignin**	**Effects on Cellulose**	**Effects on Hemicellulose**	**Negative Effects**
Dilute acid	Redistribution	Some depolymerization	80-100% solubilization	Salting
Steam explosion at high [solids]	Redistribution	Some depolymerization	80-100% solubilization	Cost of steam
Hydrothermal at low [solids]	20-50% solubilization	Some depolymerization	80-100% solubilization to oligomers	Lignin toxicity
Organic solvents in water	50-95% solubilization	Not indicated	Approaching 100% solubilization	Lignin toxicity
Ammonia fiber explosion	10-20% solubilization	Some decrystallization	10-20% solubilization	Salting, some lignin toxicity
Strong alkalai	≥ 50% solubilization	Some swelling and crystal structure changes	≥ 50% solubilization	Lignin toxicity Salting
Lime	40±% solubilization	Not indicated	≤ 30% solubilization	Lignin toxicity Salting

Once the lignocellulose is physically and chemically disrupted, the toxic phenolics from lignin solubilization (Larsson *et al.* 2001) are removed (at additional cost), and the hemicellulose and cellulose are broken down into mono-saccharides. The subsequent ethanolic fermentation process is largely the same as already described, although the 5-carbon sugars cannot be fermented by wild-type *Saccharomyces*.

Overall, the processing of lignocellulose is more complicated, uses more expensive consumables, and is more capital-intensive than dealing with sugar or starch feedstocks. These additional expenses explain why lignocellulose is not currently the preferred substrate for ethanolic fermentation, in spite of the fact that lignocellulose is a much cheaper and more abundant feed stock for ethanolic fermentation. These difficulties and expenses offer the greatest opportunities for improvements through research and development, however.

Energy and Carbon Balance

From geopolitical, economic, and environmental perspectives, it is beneficial if the fuel value of ethanol exceeds the energy expended in its production. Geopolitically, if we can supply our liquid fuel needs domestically, it is good for our trade balance and limits the extent to which we may get militarily involved over energy-related concerns. It benefits us economically if we can produce liquid fuel at a reasonable cost, without increasing the costs of other goods, and without increasing our trade deficit. Likewise, it is an environmental benefit if we can use solar energy to help produce liquid fuel, as long as it is accomplished without degrading our cropland and increasing our CO_2 emissions.

Ethanol, which is produced primarily from corn in the U.S., is a controversial subject when energy balance is concerned (Wallace 2006). Reports on the true fuel value of the ethanol relative to fossil energy vary over the range of 0.7-1.4, with arguments over that range centering on energy credits for coproducts and energy embodied in equipment (Table 2). Some studies have found that the fossil energy inputs for ethanol production have been higher than (Pimentel 2003) or approximately equal to (Patzek *et al.* 2003) the fuel value of the resulting ethanol. Most studies, however, have found the fuel value of the ethanol to be somewhat greater than the fossil energy inputs required to produce the ethanol (Graboski 2002, Hill *et al.* 2006, Farrell *et al.* 2006). This consensus energy gain is fairly modest, however, with approximately 1.2-1.4 units of energy in ethanol fermentation products (e.g. ethanol + distillers grains) resulting from one unit of fossil energy input.

Even if the energy balance of producing ethanol from corn is greater than 1.0, and is geopolitically and economically advantageous, the environmental benefits of the process are less clear. Fossil energy in the form of coal and/or natural gas is typically used to power the ethanol production facility, with additional liquid fuels being involved in producing and transporting the corn. Corn is a very energy- and chemical-intensive crop, with natural gas being used to produce nitrogenous fertilizers, and petroleum products used to produce pesticides (Patzek *et al.* 2003, Pimentel 2003). In producing ethanol from corn, the relatively large fossil energy inputs, much of which comes from coal, produces approximately as much CO_2 and possibly more nitrogen oxides (NO_x) as would be released if gasoline from petroleum were used. Additionally, ethanol containing fuels often have higher volatile emissions (Hill *et al.* 2006).

Corn is not the best feedstock for ethanol production based on energy balance or environmental effects. Moreover, the potential for corn to supplement our transportation fuel is limited. As an extreme example, even if the entire U.S. corn crop (11 billion bushels) were converted to ethanol (approximately 27 billion gallons, USDA 2007), this would be equivalent to 19 billion gallons of gasoline, or 13 percent of our gasoline usage of 141 billion gallons in 2005 (EIA 2007). Although corn production can be increased somewhat and improvements in technology might marginally increase the ethanol yield from corn, using the majority of the corn crop for fuel would have negative repercussions on food prices and exports (Elobeid *et al.* 2006, Tokgoz *et al.* 2007). This scenario illustrates that ethanol from corn is, at best, a small part of the solution to our energy situation.

The geopolitical, economic, and environmental benefits of fuel ethanol can only be fully realized with cellulosic (lignocellulosic) material as the feedstock. Perlack *et al.* (2005) estimate that 1.3 billion tons of cellulosic material can be sustainably harvested in the U.S., a quantity sufficient to displace 30-40 percent of current petroleum use. The energy ratio (ethanol energy output/fossil energy input) possible with cellulose conversion to ethanol is estimated to be as high as 10.3, compared to 1.2-1.4 with corn (Perlack *et al.* 2005). The difficulty (cost) of producing ethanol from cellulosic material currently limits this approach, however.

Ethanol as Fuel

Gasoline and Ethanol Blends

As already mentioned, ethanol has a history as a transportation fuel as old as the internal combustion engine. With developments over the past several decades, the use of ethanol as a transportation fuel has been increased. The revival of ethanol in the U.S. is tied to two events, both in the 1970's. These were the advent of catalytic converters, which required the removal of tetraethyl lead as an octane-booster, and the 1973 Arab oil embargo, which limited gasoline supplies. Thus, ethanol was added both to boost octane in unleaded gasoline and as a gasoline extender (McCormick and Parish 2001, EIA 2007).

Although oxygenated gasoline had previously been in use in many areas for the purposes of enhancing the octane rating, the Clean Air Act of 1990 mandated the use of reformulated (oxygenated) fuels to reduce smog-forming mobile (automotive) emissions in polluted areas (EIA 2007). Methyl *tert*-butyl ether (MTBE), synthesized from petroleum, and ethanol from fermentation were the compounds used most abundantly according to availability, local regulations, and cost (including tax advantages). MTBE was relatively quickly found to be a widespread groundwater contaminant, since it is both water soluble and difficult to biodegrade (Hanson *et al.* 1999, Steffan *et al.* 1997). In 2000, the EPA moved to reduce and eliminate the use of MTBE in gasoline (EAI 2007), making ethanol the main oxygenate in reformulated gasoline. Since 1980, all gasoline-powered vehicles produced for sale in the U.S. have been designed to run on 10 percent ethanol (E10), and all currently produced gasoline-powered vehicles can run on 15 percent ethanol (E15) without modification (EPA, 2006). As has been described, flex-fuel vehicles (FFV) capable of running on M85 (methanol) were introduced in the early 1990's. Similar vehicles using 85 percent ethanol: 15 percent gasoline (E85) are currently being promoted (EPA 2006).

The Navy and Marine Corps installations are operating many alternative fuel vehicles that use E85 (Table 3). As of 2006 the Navy and the Marine Corps have used over 118,000 gallons of E85 (Table 4).

As with methanol, petroleum fuels containing ethanol have a mileage penalty proportional to its ethanol content because ethanol has a 30-40 percent lower energy density than the petroleum it replaces (Figure 1 and Table 2). For E15, the theoretical penalty is a relatively minor 5 percent, perhaps not enough to be noticed by the average driver. Moreover, modern engine controls can mitigate this mileage penalty, to some degree, by modifying the ignition timing. For E85, the theoretical mileage penalty is 26 percent. Engines optimized to run on pure ethanol (Brusstar *et al.* 2002), or even E85, can greatly mitigate or eliminate this mileage penalty by having a higher compression ratio, giving more power for the same amount of fuel. Ethanol-optimized engines, however, do not have the flexibility to use normal gasoline, and no vehicles optimized for running on E85 are currently in mass production.

Diesel and Ethanol Blends

Ethanol blends with diesel are currently under investigation. Ethanol-diesel blends up to 15 percent (ED15) are being considered for use in modern diesel engines. Diesel engines already operate under high compression and, in contrast with gasoline engines, have little room for efficiency improvements. Thus, the approximately 40 percent lower volumetric energy density of ethanol (30 MJ/kg or 24 MJ/L, Figure 1 and Table 2) necessarily means 6 percent lower power and mileage with ED15, compared to regular diesel (approximately 47 MJ/kg or 40 MJ/L). Any compromise in power or mileage is a serious tactical concern for the military.

A main issue is the solubility of ethanol in diesel, with phase separation and safety being critical concerns. Ethanol up to 15 percent forms a microemulsion in diesel, but this can phase-separate at temperatures lower than 20°C (Fernando and Hanna 2004). Additives (surfactants) keep ethanol and diesel mixes from bulk separation, but adsorption of water can still cause separation. Biodiesel (discussed later) can be an effective stabilizer for ethanol in diesel (Fernando and Hanna 2004). Bulk phase-separation of the fuel is to be avoided, as it can result in engine failure and/or permanent damage. Given that much of the Navy's fuels are transported in seawater-compensated tanks, water adsorption and subsequent separation of ethanol-diesel emulsions would be a severe problem.

In addtion to the seawater storage issue, ethanol-diesel microemulsions pose serious safety concerns. The headspace of a tank at 20°C with ED15 will contain approximately 6.5 percent ethanol in air, an explosive mixture needing only a spark to ignite (Waterland *et al.* 2003, Weyandt and Janssens 2003). Because gasoline headspace at 20°C is too rich to ignite, ED15 might be more dangerous than gasoline. Because of its low flash point, ED15 does not meet the American Society for Testing Materials (ASTM) standards for diesel fuel and cannot be sold to the general public as diesel fuel (McCormick and Parish 2001, Waterland *et al.* 2003). "Real world" use to date has involved centrally-fueled commercial vehicles, which have not experienced any catastrophic accidents (*i.e.* explosions) with ethanol-diesel blends, in spite of the recognized risk (Waterland *et al.* 2003).

In laboratory testing various commercial fuel tanks and flame arrestors, Wyandt and Janssens (2003) found multiple failures of flame arrestors and tanks. Many flame arrestors simply failed by allowing an explosion to propagate into the tank. Others were able to arrest the flame, but unacceptably restricted the fill rate of the tank, which would lead to fuel spills. Fuel spills are, of course, another safety risk. In addition to effective flame arrestors being recommended in all tankage that will hold ethanol-diesel, the report suggests that a "blow-out panel" be incorporated into tanks, so damage from any explosion would be minimized.

Because of the microemulsion safety issues (McCormick and Parish 2001), ethanol-diesel blends are not practical Navy fuels, even for non-tactical uses. Moreover, in tactical uses, the ethanol-diesel blend would be incompatible with seawater compensated fuel storage, as the ethanol would dissolve into the seawater. Even if safety and storage concerns were put aside, an ethanol-diesel blend would be problematic for tactical uses, given a greater logistical support burden proportional to the lower energy density of the ethanol.

The safety and energy density issues are probably similar for ethanol blends with jet fuel, though there is no information to be found on such blends. It is conceivable that blending ethanol with kerosene might be slightly less problematic than with diesel, given that kerosene is a lighter petroleum fraction than diesel. This would need to be investigated, however. Even if an ethanol-jet fuel blend resulted in a true solution, which would improve the safety of the product, three issues would remain, however. First is the issue of whether the resulting blend could meet the 60°C flash point required for JP-5. The second issue is the lower energy density of ethanol (30 MJ/kg, 24 MJ/L) relative to JP-5 (43 MJ/kg, 35 MJ/L), which would proportionately decrease the aircraft range and/or power, and increase the logistical burden. The third issue is the compatibility of ethanol-containing fuels with seawater.

Economic and Technological Gaps

The use of ethanol as motor vehicle fuel substitute for gasoline is essentially governed by economic issues, with some adjustments for political considerations and public perception.

Fundamentally, if ethanol can be produced more cheaply than gasoline, then it will displace it to the extent technologically possible and according to the economics of supply-and-demand. Currently ethanol is competitive with gasoline only because of federal and state tax credits of \$0.51+ per gallon and mandates for ethanol in reformulated gasoline. Tax credits probably cannot be extended without modification indefinitely, as those taxes are designated and needed for road maintenance and construction. Rather, current tax credits are temporary measures designed to stimulate the infrastructure required for ethanol production (Tokgoz *et al.* 2007).

The production of ethanol from corn is, and will continue to be, limited to a small fraction of our current transportation needs. Although production of ethanol from corn will continue to be important for the foreseeable future, the energy balance and environmental "benefits" are fundamentally limited. Production of ethanol from lignocellulosic materials promises a much better energy balance and lower CO_2 emissions, although this is currently more expensive. Approaches to improving ethanol production can be divided into general approaches and those specific to producing ethanol from cellulosic materials.

General Approaches to Improving Ethanol Production

There are several general approaches for improving the efficiency of ethanol production. These approaches are also broadly applicable to the production of butanol (discussed later). One approach is to increase the thermal tolerance of bacteria and yeast that produce ethanol. Increased thermal tolerance could mean a shorter batch time from a faster reaction rate, and would both decrease the cost of cooling the fermentor and the cost of distillation (Jones and Ingledew 1994). When dealing with cell-free approaches for starch or (hemi)cellulose hydrolysis, enzymes with higher optimum temperatures can be easier to purify. They can tolerate higher substrate concentrations, and often have higher reaction rates (Vieille and Zeikus 2001).

A second approach is improved tolerance to low pH. Given that starch and cellulosic materials are often hydrolyzed with acid, organisms that tolerate a lower pH would avoid salting and deleterious product formation from pH adjustments. Tolerance both to low pH and high temperatures would decrease the risk of contamination as most contaminating organisms grow best at moderate temperatures and neutral pH, although some common industrial fermentation contaminants (*Lactobacillus* spp.) are tolerant to low pH (Narendranath *et al.* 1997, Chang *et al.* 1997). A difficulty in these approaches is that thermal stress and ethanol toxicity are additive or even synergistic (Demain *et al.* 2005), and the yeast *S. cerevisiae* is already fairly tolerant of low pH.

A third general method to improving ethanol production is to increase the cultures' tolerance to dissolved solids, such as salts resulting from substrate processing and pH adjustments. This approach can improve the batch yield, with associated cost savings (Jones and Ingledew 1994). The difficulty here is much as with thermal and pH stress, with ethanol toxicity enhanced by higher dissolved solids concentration.

A fourth general approach is to increase the ethanol tolerance of cultures. Producing ethanol to higher concentration improves the batch yield and lowers the cost for distillation. High yielding strains of *S. cerevisiae* can tolerate 15-20 percent ethanol, but ethanologenic bacteria can only tolerate 3-4 percent ethanol. Metabolic activity (ethanol production rate) slows as the ethanol concentration increases, so the batch turnaround time must be factored into this consideration. For example, it is probably more profitable to design for 10 percent ethanol and have a quicker turnaround time for the fermentation infrastructure. The additional energy cost of distilling 10 percent *vs.* 15 percent ethanol may be secondary to the longer time required to ferment additional sugar to additional alcohol.

Improving Ethanol Production from Lignocellulosic Materials

Improving ethanol production from lignocellulosic materials has three basic approaches. The first approach is improved ability to degrade crystalline and semi-crystalline cellulose into glucose monomers. The rate-limiting step in ethanol production from cellulose is hydrolysis of the cellulose (Demain *et al.* 2005). The second approach is the ability to break down hemicellulose and to ferment the variety of 5-and 6-carbon sugars of hemicellulose into ethanol. The third approach is improved tolerance to lignocellulosic hydrolysis products like substituted phenols (Larrson, *et al.* 2001) and caramelized sugars. Given that lignocellulose is composed of 35-50 percent cellulose, 20-35 percent hemicellulose, and 5-30 percent lignin, these approaches are complimentary. Only when these approaches are combined can the full potential of lignocellulosic ethanol be realized.

Potential improvements in lignocellulosic ethanol production are likely to come from genetic engineering of microorganisms. Some bacteria, such as *Zymomonas mobilis*, can efficiently produce ethanol (Wood and Ingram 1992). Others, such as certain *Clostridium* species can break down cellulose or hemicellulose and produce (some) ethanol (Demain *et al.* 2005). Some fungi can break down cellulose, and the fungus *Trichoderma reesei* is used in some processes for this purpose, producing glucose for the yeast, *S. cerevisiae,* to ferment to glucose (Demain *et al.* 2005).

Although some seek to combine several processes in a single organism that can, for example, take cellulose and efficiently ferment it to ethanol, using genes from multiple organisms (Wood and Ingram 1992) is very complicated. The cellulose-degrading enzymes only function extracellularly and, thus, require the engineering of secretion pathways. Most approaches are less complicated. Two common approaches are 1. to engineer *S. cerevisiae* for a greater range of substrates and 2. to manipulate the biochemistry of the (hemi)cellulolytic *Clostridium* species to produce more ethanol with higher efficiency.

Yeast (*S. cerevisiae*) cultures capable of using 5-carbon sugars as ethanolic fermentation substrates have been produced (Becker and Boles 2003). In many cases this approach also requires designing appropriate transport mechanisms for getting the 5-carbon sugar into the cell (Eliasson *et al.* 2000). As the metabolism of the wild-type yeast is modified with new biochemical pathways, unintended and undesired metabolic effects and fermentation by-products can result (Jeppsson *et al.* 2002). An overriding difficulty in this approach is the genetic instability of such constructions, most of which involves adding bacterial (prokaryotic) genes to a eukaryote (Eliasson *et al.* 2000).

Clostridium species are obligate anaerobes, some of which are thermophilic and can break down cellulose (*Clostridium thermocellum*) and hemicellulose (*Clostridium thermosaccharolyticum*) to ethanol and other products. The approach of manipulating *Clostridium* species to produce more ethanol has several advantages, outlined by Demain *et al.* (2005). Most of these benefits are based on these organisms growing well at 60°C (thermophiles), meaning less opportunity for the fermentors to become contaminated, lower cooling costs, and less energy required for distillation. One major issue is that *Clostridium* species have is low efficiency in ethanol production and low tolerance to ethanol (approximately

1-2 percent) at optimum growth temperatures (Demain *et al.* 2005). *Clostridium* cultures with somewhat enhanced capabilities have been selected through mutagenesis, but a good understanding of these mutations and their stability has not been achieved (Lynd *et al.* 2002). Similarly, a genetic system suitable for direct and precise genetic manipulations does not exist for *Clostridium* species, unlike for the familiar *Escherichia coli*. The development of a genetic system should make the engineering of a *Clostridium* strain capable of producing ethanol from cellulose possible.

Potential for Carderock Division in Ethanol Research, Development, Testing, and Evaluation (RDT&E)

The production and use of ethanol as a transportation fuel in the U.S. has both great promise and challenges. As a tactical military fuel, however, ethanol has serious drawbacks regarding safety, storage conditions, and energy density, compared to current petroleum based fuels. Even if safety and storage issues could be addressed, as they must be for the civilian diesel market, the lower energy density of ethanol would necessarily increase the logistical burden of supplying fuel. Ethanol is not useful as an alternative tactical fuel for the U.S. Navy for these reasons. Ethanol, as E10 and E85, is already being used by the Navy as a non-tactical fuel, however (Table 3). As with methanol, there is little justification for the Carderock Division to be involved in any RDT&E with regard to ethanol as an alternative transportation fuel.

Butanol

Introduction

The properties and suitability of butanol as an alternative fuel are discussed. The discussion includes the applicability for use in gasoline and standard diesel engines in nontactical light-duty vehicles and in tactical platforms requiring Navy distillates. Butanol as we will be discussing here is 1-butanol or *n*-butyl alcohol. Butanol is typically produced from petrochemical starting materials. It is a common industrial and chemical laboratory solvent and reactant. Butanol can also be produced using various fermentation processes of biomass feedstocks and is termed bio-butanol. To date, butanol (or bio-butanol) has not been produced commercially as a transportation fuel. However, butanol has many properties that make it potentially more attractive than ethanol as an alternative fuel. Butanol can be produced from the same biomass feedstocks as ethanol including corn, sugar cane, sugar beets, and various fast growing grasses. The potential for butanol to be an environmentally friendly or “green” fuel is great. Like the other bio-fuels, carbon dioxide from the atmosphere and solar energy are used as the carbon and energy sources for growing the plants. Butanol is soluble in gasoline, ethanol, diesel, and biodiesel. It could be used as an additive at any ratio to fuel systems with these components. Butanol has a higher combustion energy content and flash point than ethanol. These properties make butanol attractive as a gasoline additive or full replacement. Butanol has an energy density similar to biodiesel and a sufficiently high cetane number (critical for diesel ignition) to be useful as a diesel or biodiesel additive. It has a lower freezing point than biodiesel and could be used to improve low temperature performance.

Critical Properties

Many critical butanol properties are given in Table 2. A few properties will be discussed in a bit of detail. The energy density of butanol by weight is nominally 37 MJ/kg. This is the heat content per unit mass generated upon complete combustion of the material. As a property of a fuel in an engine, this value is greatly responsible for the fuel efficiency or range of a vehicle. If an engine has a constant efficiency, the fuel with the greatest energy density will provide the best fuel efficiency. One is generally limited by the size of the fuel tank so range is dictated by the fuel's energy per unit volume. Butanol has a density of 0.81 g/cm^3. Therefore, the energy density in terms of volume is 30MJ/L. The energy density (by mass or volume) of butanol is 33 percent greater than for ethanol. Compared to biodiesel, butanol has nearly identical energy density by weight but is 10 percent less by volume. Compared to gasoline, butanol has 20 percent less energy by weight and 8 percent less by volume as shown in Figure 1.

The flash point of butanol is 27°C. This is dramatically higher than gasoline which has a value of about -40°C. It is lower than diesel, particularly DFM that has a flash point greater than 60°C. The flash point is a property related to sustained ignition of the material. The Navy is particularly concerned with flammability and fire safety issues aboard confined ship spaces. Pure butanol or DFM blends with appreciable amounts of butanol would be unacceptable for Navy use. The possibility exists that blends of butanol and biodiesel, that has flash points of 130°C or greater, would yield an acceptable blended flash point. Studying blends of butanol, biodiesel, and DFM could be an area worth further consideration.

The cetane number for butanol is 25. This is a value related to the ignition of fuel in diesel engines. A value of 42 or greater is required for DFM. Appreciable quantities of butanol in a butanol-DFM blend will most likely drop the cetane number below the currently accepted number. However, a retuning of the engines would probably allow for lower acceptable cetane values.

The freezing point of butanol is –90°C. The requirement for JP-5 is –46°C. No requirement is stated for DFM. The required pour point of DFM however is –6°C. The value for butanol is undoubtedly lower. This would allow for butanol blends to operate in colder environments. If biodiesel becomes a candidate to be blended with DFM, butanol could be considered as an additional additive to improve cold temperature performance.

The corrosivity of butanol to engines, storage containers, and pipelines is significantly less than for methanol or ethanol. This is due to the reduced solubility of water in butanol compared to that in the other alcohols. Water is only slightly soluble in butanol, whereas water and ethanol are soluble in all proportions. This would allow for butanol to be transported in existing pipelines.

A comparison of the fuel properties provided in the MILSPECs for DFM and JP-5 to the known properties of butanol was made. Table 7 outlines the tested properties of DFM and the acceptable values. In the last column a short description of how butanol or 85/15 DFM to butanol blend would compare to the acceptable values is given. A similar comparison to JP-5 is given in Table 8. Only a few butanol properties are explicitly known. Some values, such as the distillation numbers are not applicable. Other properties, such as color, clarity or trace metal values might be one thing for reagent grade butanol, but significantly different for bio-butanol products. At this point there are no standards to which bio-butanol must conform, so it is difficult to compare most of the properties. If bio-butanol becomes a mainstream commercial fuel, many of these properties will certainly be specified and could be compared to MILSPEC values.

Production Capability

The predominant commercial method for producing butanol involves the conversion of syngas and propylene to n-butanol using what is known as the Oxo process. Production is primarily in Texas and Louisiana and is intimately tied to the petroleum industry. The butanol production capacity for the United States in 2002 using this process was approximately 2.4 billion pounds (355 million gallons) at a cost of about $0.55 per pound ($6.42 per gallon) delivered in tanks (The Innovation Group, 2007).

Bio-butanol can be fermented from any of the biological feedstocks used to produce ethanol. These include such materials as corn, sugar cane, sugar beets, whey lactose, wheat straw, and various grasses such as switchgrass.

Butanol can be produced via various fermentation processes. The first and most common process is one that produces acetone, butanol, and ethanol (A.B.E. process) using the bacterium *Clostridium acetobutylicum* (Jones and Woods, 1989). This process was developed in 1916 and used primarily for the acetone that was needed for the production of explosives. The traditional yield of butanol to acetone to ethanol using this process is 6:3:1 by volume. After the 1940's, acetone and butanol production from petroleum products became favorable.

With the renewed interest in producing butanol as a bio-fuel, other methods that improve upon the traditional A.B.E. process for butanol production have been made. One method uses *Clostridium beijerinckii* BA101in a batch fermentation process to produce butanol with significantly higher yields compared to traditional processes (Formanek, Mackie, and Blasckek, 1997). This effort utilized corn products as the biomass. Other workers have investigated the fermentation of wheat straw using *Clostridium beijerinckii* (Qureshi, Saha, and Cotta 2007).

The lack of a process that produces butanol nearly exclusively was presumably one of the contributing factors that favored ethanol production as the bio-alcohol fuel of choice. An encouraging new process was patented by Environmental Energy Inc. (EEI), now ButylFuel LLC (BFL), in 1998 (Ramey 1998). This process uses *Clostridium tyrobutyricum* to produce butyric acid that is subsequently converted to butanol. The production of ancillary products is greatly reduced. BFL used this process to produce quantities of butanol from corn. They claim the production of 2.5 gallons of butanol per bushel out of a theoretical limit of 2.8 (www.butanol.com). A traditional process would produce approximately 1.3 gallons per bushel. BFL claims to produce 24 percent more energy per bushel corn than from standard ethanol fermentation. In addition to the direct butanol energy, 18 percent of the ethanol equivalent of energy is produced in the form of recoverable hydrogen (ButylFuel, LLC. 2007). Assuming that the energy expenditure to process a bushel of corn to butanol is nearly equivalent to that in ethanol production, butanol is much favored over ethanol in terms of net energy output. Cost estimates for producing butanol from corn using the BFL process is $1.20 per gallon (Table 5). BFL has generated plans to produce butanol from whey lactose, a cheese production byproduct. Using waste products, such as whey, cost estimates as low as $0.85 per gallon have been made.

Table 7. Butanol compared to DFM requirements

PROPERTY	DFM Requirement MIL-DTL-16884L	85% DFM 15% Butanol
Appearance, at 25°C or ambient whichever is higher	Clear, bright, and free of visible particulates	No reason for reduced clarity
Distillation: 10% Point, °C 50% Point, °C 90% Point, °C (max) End Point, °C (max) Residue + Loss, % vol. (max)	 Record Record 357 385 3.0	Not applicable
Flash Point, °C (min)	60	**27 for 100% BuOH Good chance of passing**
Carbon Residue on 10% bottoms, wt. % (max)	0.14	Unknown
Sulfur Content, wt. % (max)	0.5 16/	Unknown
Ignition Quality: Cetane Number, (min) Cetane Index, (min)	 42 43	**25 for neat BuOH Blend probably exceeds**
Viscosity, 40°C, mm2/second	1.7 – 4.3	3.6 for 100% BuOH
Acid Number, mg KOH/g (max)	0.30	Unknown
Ash, wt. % (max)	0.005	Unknown
Corrosion, at 100°C (max)	No. 1	Unknown – low water sorption minimizes corrosivity
Trace Metals, ppm (max): Calcium Sodium + Potassium Lead Vanadium	 1.0 1.0 0.5 0.5	Unknown
Demulsification, at 25°C, minutes (max)	10	Unknown
Density, at 15°C, kg/m3 (max)	876	810 for 100% BuOH
Cloud Point, °C (max)	-1	Could decrease
Color, (max)	3	Should have low color
Particulate Contamination, mg/liter (max)	10	Don’t expect particulates
Pour Point, °C (max)	-6	Could decrease
Hydrogen Content (min %)	12.5	13.6 for 100% BuOH
Additive Names and Dosages	Record	Record
Storage Stability, Total Insolubles, mg/100 ml (max)	3.0	Unknown

Table 8. Butanol compared to JP-5 requirements

PROPERTY	JP-5 Requirements MIL-DTL-5624U	85% JP5 15% Butanol
Sulfur, total, mass percent, max	0.30	Unknown
Flash point, °C, min	604/	**27 for 100% BuOH Good chance of passing**
Total acid number, mg KOH/g, max	0.015	Unknown
Distillation temperature, °C Initial boiling point 10 percent recovered, temp 20, 50 and 90 percents recovered, temp End point, max temp Residue, vol %, max Loss, vol %, max	 Report 205,max Report 300,max 1.5 1.5	Not applicable
Copper strip corrosion, 2 hr at 100°C (212°F), max	1	**Unknown**
Color, Saybolt	Report	Should have low color
Aromatics, vol percent, max	25.0	None present
Sulfur, Mercaptan, mass percent, max Or Doctor test	0.002 Negative	Unknown
Hydrogen content, mass percent, min	13.4	13.6 for 100% BuOH
Smoke point, mm, min	19.0	Unknown
Thermal stability: Change in pres. drop, mm of Hg, max Tube deposit code, less than	 25 310	Probably no effect
Existent gum, mg/100 mL, (max)	7.0	Unknown
Particulate matter, mg/L, (max)	1.0	Unknown
Filtration time, minutes, (max)	1513	Unknown
Water reaction interface rating, (max)	-------	-------
Micro Separometer rating, (min)	14	Unknown
Fuel system icing inhibitor, vol % (range)	0.10-0.15	Not applicable
Fuel electrical conductivity, pS/m (range)	------	-------
Density, at 15°C, kg/L, (range)	0.788- 0.845	0.810
Vapor pressure, at 37.8°C (100°F), kPa (range)	-------	-------
Freezing point, °C, (max)	-46	-90 for 100% BuOH
Viscosity, at -20°C, mm2/s (max)	8.5	3.6 for 100% BuOH
Heating value, MJ/kg, (min)	42.6	Slight decrease (100% BuOH=37)
Calculated Cetane Index 7/	Report	Unknown – 100% BuOH=25

No other notable source of bio-butanol has been found. A DuPont-BP petroleum joint venture into alternative fuel production has advertised intent to produce butanol from sugar beets in the United Kingdom (DuPont 2006).

At this time there is very little production capability for butanol as a transportation fuel. Presumably, much of the technology and facilities required for butanol fermentation is similar to that for ethanol production. If an emphasis was made to move towards butanol and away from ethanol, ethanol facilities could be converted to butanol production.

Suitability as a Fuel Source

From a property standpoint, butanol seems to be superior to ethanol for use in alcohol-gasoline blends. The most significant factor is its energy content. It has an energy density approximately 30 percent greater than that of ethanol. This is an advantage for the driver who will experience greater fuel economy and range, especially at the higher alcohol levels. Because of the greater energy content derived from a common source, such as a bushel of corn, butanol has an advantage from an environmental perspective. This difference is exaggerated when considering the recoverable hydrogen that is generated in butanol production. Less energy will be needed to produce a usable BTU of fuel. The reduced corrosivity of butanol makes it very suitable as an alternative fuel. Compared to ethanol, it is expected to be less harmful to automotive engines and fuel systems. A major advantage is that the reduced corrosivity allows it to be transported in existing fuel pipelines. Gasoline engines have been shown to operate on 100 percent butanol. One example was found comparing a standard gasoline engine running on 100 percent butanol and running on gasoline (ButylFuel, LLC 2007). In this test, David Ramey of Environmental Energy Inc. drove an unmodified 1992 Buick Park Avenue 10,000 miles across the United States on pure butanol and achieved a fuel economy of 24 mpg.

Standard gasoline performance in that car was 22 mpg. The mileage instead of being 8 percent lower than gasoline was about 9 percent better, showing an improved efficiency in that vehicle. Butanol shows promise as a suitable gasoline additive or replacement.

Butanol could also be used as an additive to commercial diesel fuels. It is soluble in all proportions in diesel fuel and could be blended into diesel at appreciable levels. It has a cetane number of 25 and diesel-butanol blends should have a sufficiently high cetane number for optimal combustion in diesel engines. Various studies and patents of diesel-butanol blends showing adequate performancehave been made (Bhattacharya, et. al. 2004), (Elsea and Etheridge, 1982)

Incorporation of butanol into Navy distillates is somewhat less attractive. The 27^{o}C flashpoint is significantly below the 60^{o}C requirement and significant fractions of butanol would produce a flash point below the required temperature. This alone would preclude significant use of butanol. Blends of high flashpoint biodiesel and butanol with DFM might prove acceptable. The significantly lower energy per unit volume of butanol compared to DFM also makes it unattractive as an alternative fuel. This penalty could be suffered in civilian use, but considering mission critical needs and fuel logistics, it is one less likely to be tolerated by the Navy. Another issue is storage on ships where the fuel is in contact with seawater. Butanol is solubile in water up to eight percent solution. This could result in extraction of butanol from the fuel mixture and would be undesirable.

If butanol became available on a large transportation scale, such as ethanol has, it would be suitable to be used alongside of or in place of ethanol and biodiesel in nontactical, light-duty vehicles. It is significantly less attractive for incorporation into Navy distillates.

Technology Gaps and Areas for NSWC S&T Investment

Many of the properties of butanol pertinent to long term fuel use need to be investigated. For butanol to be used as a substitute or significant component in gasoline or diesel fuel its effect on fuel systems, engine and seal wear, *etc*. need to be studied. Standards for bio-butanol as a transportation fuel do not exist. It is likely that various butanol products could have significantly different properties, including overall purity, trace metal content, particulates, clarity, and water content. These could affect combustion properties, long term stability, corrosion, and emissions. Properties of this sort would need to be to be studied in detail and standards would need to be established. For butanol to be incorporated into the Navy distillates, the properties of those blends that pertain to the existing MILSPECs would need to be investigated.

As an NSWC S&T effort, investigating the addition of butanol to biodiesel to improve the low temperature performance of biodiesel is of interest. Details of this are given in the biodiesel section of this report.

Biodiesel

Introduction

Biodiesel is produced from domestic renewable resources such as plants and animals for the vegetable oil and animal fat, respectively. Biodiesel and blends with petroleum diesel can be burned in a combustion ignition (diesel) engine generating fewer pollutants and with greater efficiency. Several vehicle manufacturers (New Holland, Daimler Chrysler, and Artic Cat) have approved biodiesel blends for use on many commercial vehicles.

There is a research effort on the system impact of fuels containing up to five percent biodiesel (Turner, L. 2007). The use of biodiesel as a tactical fuel is not completely ruled out. The long term use and effects of biodiesel on ship engines may require further studies.

Evaluation of the suitability of biodiesel

Biodiesel is classified as an alternative fuel to petroleum diesel and produced from domestic, renewable resources, which implies a possible reduction in foreign petroleum imports. Biodiesel is refined from animal fat or vegetable oil, e.g. soybean. It can be used pure or mixed in any proportion with No.2 diesel or No. 1 diesel, where the most common blend is 20 percent biodiesel and 80 percent diesel by volume. They are designated as B100 for pure/neat biodiesel and B20 for a 20/80 blend. Both the pure and blended biodiesel have been tested in compression-ignited (diesel) engines with little or no modification to the engine. Biodiesel, that meets ASTM D6751 – 06b and is legally registered with the Environmental Protection Agency, is a legal motor fuel for sale and distribution.

Biodiesel is a promising diesel replacement fuel for Navy use for land vehicles, diesel to electric power generation, and diesel ships. To determine the feasibility of biodiesel for Navy use, a comparison is made between the MILSPEC requirements for Diesel Fuel Marine (DFM), also referred to as F-76, with the requirements from the ASTM Standard for biodiesel. The specific requirements for DFM are from Fuel, Naval Distillate (MIL-DT-16884L) and for biodiesel are from Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels (ASTM D6751 – 06b).

In this comparison, the specific property values for biodiesel that are compliant with DFM are presented in Table 9. Several properties of biodiesel are not within the specification for DFM and shown in Table 10 as the “non-compliant” values. There are also several properties for DFM that cannot be compared with biodiesel, because they were not measured for biodiesel. These properties are referred to as “not-known” values and are presented in Table 11. Both the flash point and cetane values of biodiesel are greater than or comparable to the values with DFM. A high flash point is needed to provide assurance to the user that fuel will not ignite in confined spaces, such as ship compartments. The cetane number is measure of the ignition quality of the fuel. The sulfur content of biodiesel is below the DFM limit. In the non-compliant requirements (Table 10), the viscosity at 40^{o}C of biodiesel is slightly higher than DFM. This may have an effect on the transporting of the fuel through fuel lines in the diesel engine. The ash content for biodiesel is higher than DFM, which may increase particulate emissions. In the not known requirements (Table 11), the pour point for biodiesel would be important to determine and compare with DFM of -6^{o}C (maximum). The pour point provides an indication of low operating temperature use without pre-heating in the fuel tank and lines. The corrosion measurement for DFM is done at 100°C as compared to biodiesel at 50°C. This test serves to measure the possible corrosion of copper and brass or bronze parts in the fuel system. The presence of acids or sulfur-containing compounds can tarnish the copper test strip, thus indicating the possibility for corrosion of the engine and associated parts. As shown in Table 9, the sulfur content in biodiesel is at least one order of magnitude lower than DFM.

Table 9: Compliant requirements of biodiesel as compared with diesel fuel marine.

FUEL, NAVY DISTILLATE MIL-DTL-16884L 23 OCT2006			BIODIESEL ASTM D6751 - 06b		
Characteristic	Requirement	ASTM Test Method	Grade S15[a]	Grade S500[a]	ASTM Test Method
Appearance, at 25°C or ambient whichever is higher	Clear, bright, and free of visible particulates	D4176 1/	Free of undissolved water, sediment, and suspended matter		D6751-06b
Distillation:					
10% Point, °C	Record				
50% Point, °C	Record				
90% Point, °C (max)	357	D86 3/			
End Point, °C (max)	385		360 (max)	360 (max)	D1160
Residue + Loss, % vol. (max)	3.0				
Flash Point, °C (min)	60	D93 (R) 8/, D6450 8/	130 (min)	130 (min)	D93
Carbon Residue on 10% bottoms, wt. % (max)	0.14	D189, D4530 12/	0.05 (max)	0.05 (max)	D4530
Sulfur Content, wt. % (max)	0.5 16/	D4294 (R) 17/, D129, D1266, D1552, D2622, D3120, D5453 (R) 18/, D6920, D7039	0.0015 (max)	0.05 (max)	D5453
Ignition Quality:					
Cetane Number (min)	42	D613 (R) 13/	47 (min)	47 (min)	D613
Cetane Index, (min)	43	D976 13/			

[a] S15 and S500 is a designation for sulfur content to be 15ppm and 500ppm maximum.

Table 10: Non-compliant requirements of biodiesel as compared with diesel fuel marine.

FUEL, NAVY DISTILLATE MIL-DTL-16884L 23 OCT2006			BIODIESEL ASTM D 6751 - 06b		
Characteristic	Requirement	ASTM Test Method	Grade S15[a]	Grade S500[a]	ASTM Test Method
Viscosity, 40°C, mm^2/second	1.7 – 4.3	D445	1.9 – 6.0	1.9 – 6.0	D445
Acid Number, mg KOH/g (max)	0.30	D974 (R) 11/, D664	0.5 (max)	0.5 (max)	D664
Ash, wt. % (max)	0.005	D482	0.02 (max)	0.02 (max)	D874
Calcium, ppm (max)	1.0	D7111 (R), D3605	5A	5A	EN 14538
Sodium plus Potassium, ppm (max)	1.0		5	5	EN 14538

[a] S15 and S500 is a designation for sulfur content to be 15ppm and 500ppm maximum.

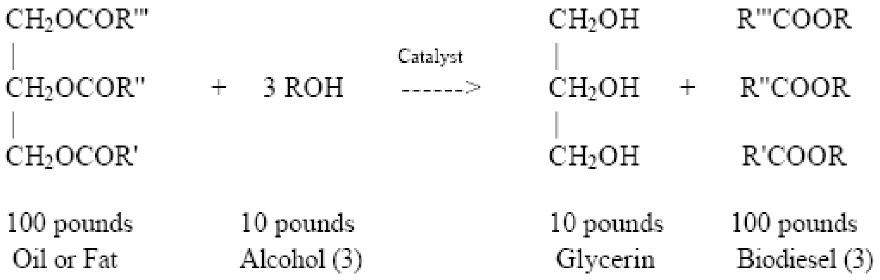
Table 11: Requirements not-known for biodiesel as compared with diesel fuel marine.

FUEL, NAVY DISTILLATE MIL-DTL-16884L 23 OCT2006			BIODIESEL ASTM D6751 - 06b		
Characteristic	Requirement	ASTM Test Method	Grade S15[a]	Grade S500[a]	ASTM Test Method
Demulsification, at 25°C, minutes (max)	10	D1401 2/			
Density, at 15°C, kg/m3 (max)	876	D1298 (R), D4052, D287			
Cloud Point, °C (max)	-1	D2500 (R), D5771, D5772, D5773 4/, D6371 5/, IP 309 6/, D4539 7/	ReportA	ReportA	D2500
Color, (max)	3	D1500 (R), D6045			
Particulate Contamination, mg/liter (max)	10	D6217 (R), D5452 9/			
Pour Point, °C (max)	-6	D97 (R), D5949, D5950, D5985 10/			
Corrosion, at 100°C (max)	No. 1	D130	3hr, 50°C No. 3 (max)	3hr, 50°C No. 3 (max)	D130

[a] S15 and S500 is a designation for sulfur content to be 15ppm and 500ppm maximum.

Assessment of the current technologies

The current production of biodiesel is done by a base catalyzed transesterification (U.S. Department of Energy Alternative Fuels 2007) of the vegetable oil or animal fats with alcohol. This process is done at low temperature (66^{o}C) and pressure (20 psi) with a conversion rate of 98 percent. A schematic of the transesterification chemistry is presented in Figure 3.



Triglyceride Alkyl Ester

Figure 3: Base catalyzed transesterification of vegetable oil to biodiesel. Adapted from National Biodiesel Board, 2007c.

The chemical process is the reaction of fat or oil (triglycerides) with an alcohol (typically, methanol) in the presence of a catalyst to produce biodiesel (methyl esters) and a co-product of glycerin. An excess amount of methanol is used to assist in rapid conversion and recovered for re-use. The catalyst is usually sodium hydroxide or potassium hydroxide, dissolved in methanol. Typical composition of alkyl esters is listed in Table 12. The viscosity of the alkyl esters is one-eighth of the viscosity of the original vegetable oil. Each ester chain retains two oxygen atoms and gives the product its unique combustion qualities as an oxygenated vegetable based fuel. Biodiesel is nearly 10 percent oxygen by weight. In contrast, petroleum diesel is made up of hundreds of different hydrocarbons in the range of 10-22 carbons with small, but variable amounts of sulfur, oxygen, and nitrogen.

Any source of complex fatty acids can be used, such as, soybean, rapeseed (Canola™ oil), corn, recycled fryer oil, and tallow to be converted to biodiesel. Approximately 55 percent of the biodiesel industry uses fats or waste cooking oil and grease. The other half of the industry is limited to vegetable oils; the least expensive is soybean oil. Currently, manufacturing plant facilities in the U.S. annually produce 1.9 billion gallons of biodiesel (National Biodiesel Board 2007d, Capacity). This represents roughly 5 percent of the 36 billion gallons on-road diesel (Energy Information Agency Annual Energy Review 2002) used in the US. There are about 105 manufacturing plants (Figure 4) with 77 plants under construction for 2007 – 2008. Several existing plants are scaling up to increase their annual production output, as an indication of the scalability. The average cost for biodiesel is about 1¢/MJ (Table5).

Table 12: Typical soybean oil methyl ester profile - molecular weight and chemical formula for each of the component esters.

Fatty Acid	Weight Percent	Mol. Wt.	Formula	Carbon No.
Palmitic	12	270.5	$C_{15}H_{31}CO_2CH_3$	C_{16}
Stearic	5	298.5	$C_{17}H_{35}CO_2CH_3$	C_{18}
Oleic	25	296.5	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3$	C_{18}
Linoleic	52	294.5	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7\ CO_2CH_3$	C_{18}
Linolenic	6	292.5	$CH_3(CH_2CH{=}CH)_3(CH_2)_7\ CO_2CH_3$	C_{18}

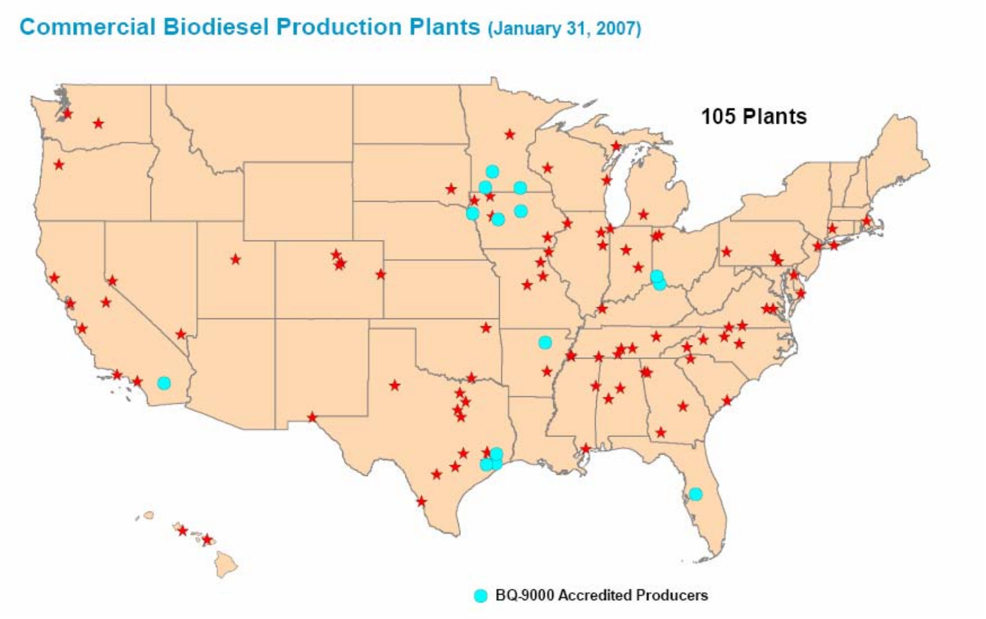


Figure 4: Location of Commercial Biodiesel Production Plants in the United States. Adapted from National Biodiesel Board, 2007d.

The energy balance for biodiesel is under contention by various researchers. The energy balance is the ratio of the energy contained in the fuel to the energy required to produce the fuel. The production energy is the summation of the energy required to grow the crop, to extract and refine the vegetable oil, to perform the esterification, and to transport it. The Institute for Local Self-Reliance (Irshad and Decker 1994) reports a ratio of 2.5 to 1 (Table 5). A net energy gain based on average practices: average soybean farm and average oil extraction, refining, and esterification facilities. This value increases to 3.2 to 1 for soybean production based on the current best agriculture and oil processing practices in the U.S., as reported by Biodiesel.org (National Biodiesel Board Foreign Oil 2007a and Sheehan *et al.* 1998). A later report (Pimentel and Patzek 2005) shows a ratio of 0.8, a net energy loss. An evaluation was made by this study to determine the difference between the two energy balances. The major difference is that the predicted energy input for growing the soybean by Irshad was significantly lower than Pimental, which resulted in a net energy gain. Several researchers (Wang 2005, Van Gerpen and Shrestha 2007) have reviewed and disagreed with this latest energy calculation. Wang offers these two points to consider: 1) “Energy balance calculations for individual energy production in their isolation could be arbitrary; results are less meaningful or could be misleading.” 2) “Decisions on pursuing certain energy products by society have not been based on their energy balance values. For example, electricity generation has a huge negative energy balance value (2.3 unit of fossil energy input for a unit of electric energy output in the U.S.). We do not question the practice of electricity generation. The quality of energy products should be taken into account in making energy choices.”

Lubricity & Engine Wear, Energy Content, Power Differences, Fuel Consumption, Stability and Storage of Biodiesel

Lubricity properties of fuel are important for reducing friction wear in engine components normally lubricated by the fuel rather than crankcase oil. Petroleum diesel fuel sold today contains sulfur and aromatics (benzene, toluene, xylene, etc.), which provide lubrication to improve engine wear. These same chemical components are toxic and volatile, causing health problems and presenting fire hazards. In 1993, the California Air Resources Board (CARB) mandated stricter laws than the Federal requirements for low sulfur, low aromatic diesel fuel. This type of fuel resulted in a decrease in lubricity and a reduction in the elastic properties of the gaskets, O-rings and seals in older engines. For many truck operators, this diesel fuel was not acceptable. A minimum level of sulfur and aromatics appears to be necessary in the fuel for lubricity (engine wear) and longevity of the gaskets and seals.

Biodiesel has been studied extensively in Europe and the U.S. for its effect on long-term engine wear, particularly with respect to those components normally lubricated by the fuel itself such as fuel pumps and injector pumps. Initial work on the lubricity of biodiesel, performed by Mark-IV Group and the Southwest Research Institute in 1994, established a clear advantage to blending biodiesel with petroleum diesel to achieve superior lubrication (von Wedel 1999). In 1993, Exxon showed that a 20 percent blend of biodiesel with petroleum diesel had significant improvements in reducing wear and friction while improving film coating ability of the blend. The lubricity properties of B20 are comparable to the lubricity additives used by Exxon. Subsequent field studies on light duty truck engines (5.9L Cummins diesel) at the University of Idaho have corroborated these results by finding an "absence of wear" and friction scars on engines broken down for inspection after a 100,000 mile road test running on 28 percent biodiesel. In a University of Idaho durability test (1,000 hour tests on small diesel engines), it was found that biodiesel was equivalent to No.2 diesel on the basis of long term engine performance and wear. The primary factors evaluated in that study were engine brake power and torque, fuel injector tip coking (carbon deposition), and engine component wear based on oil analysis.

The power output and the fuel economy of a combustion engine are related to the energy content of the fuel. The energy content of B100 (National Board Content 2007b) is 9 percent less than No.2 diesel and 2 percent less for B20 (Table 2). The energy content of DFM is assumed to be comparable to No.2 diesel. A comparison of the energy densities of liquid hydrocarbon fuels from petroleum and biomass resources are shown in Figure 1. The lower energy content is due to the presence of the oxygen in the methyl esters of biodiesel (petroleum diesel hydrocarbons have less oxygen). However, with the added oxygen, the net combustion efficiency for the blended fuel is increased, which should compensate for the slight drop in energy content. The differences would be most noticed at low rpm and high engine load when the engine would most benefit from more oxygen. Typically, for these conditions, the engine manufacturers have enhanced performance by a mechanical process, known as turbo-charging; compressing the air at the intake to enrich the oxygen content before entering the combustion chamber of the engine.

Studies conducted in the U.S. and Europe generally indicate that blends of biodiesel and petroleum diesel result in small decreases in overall power output of engines. In the 1998 study at the Southwest Research Institute, engine power in the 1997 Cummings truck engine operating on the B20 blend was found to be 98.5 percent of the power attained with low sulfur No.2 diesel. At 100 percent biodiesel, the engine generated 92 percent of the power as would be predicted by the energy density.

In the Southwest Research Institute study (1996), the fuel consumption was found to increase by only 2 percent for a B20 blend and by 14 percent for B100 in the Cummins test engine operated under transient heavy loads. Tests carried out on a Mercedes Benz diesel station wagon over a 4 year period showed that a 15 percent net decline in the mileage obtained using B100 over petroleum diesel. No change in power, acceleration or engine temperature was observed, but the engine was quieter and smoother at idle when fueled with biodiesel. Fuel consumption for a 1995 Cummings B5.9 truck engine was found to increase by 9 percent with the B20 blend, and by 18 percent with B100. Better fuel economy was noted for a 1997 Cummings N14 truck engine with a 3 percent drop in fuel consumption using B20 and a 13 percent increase with B100.

Stability during long-term storage is an important requirement for fuels used by the Navy. The term storage instability is defined as the formation of solids in the fuel that can plug fuel injectors, fuel lines, and filters of the diesel engine. The Navy desires petroleum fuels (DFM and JP5) that are capable of remaining in storage typically for a year and often much longer. On Navy ships, diesel fuels are usually stored in fuel tanks that use seawater to compensate the volume of diesel fuel used. Seawater has been shown to cause rapid deterioration of the stored fuel. In reality, many petroleum diesel fuels show some form of instability in storage.

The general rule of thumb for storage of biodiesel and blends is summarized below. Biodiesel can be stored for long periods of time in closed containers/tanks (metal and plastic) with little headspace. The containers/tanks are usually protected from weather, direct sunlight and low temperatures. Long term storage in partially filled containers/tanks, particularly in damp locations, is avoided, because water can contribute to the long-term deterioration of the both petroleum diesel and/or biodiesel. Condensed moisture can contribute to the corrosion of metal, especially with petroleum diesel that also contains sulfur. The condensed water can also support the growth of bacteria and mold that use the diesel and biodiesel hydrocarbons as a food source. These hydrocarbon-degrading bacteria and molds will grow as a film or slime and accumulate as sediment over long periods of time. The accumulation of the newly released slime and sediment can clog fuel filters causing the engine to suddenly stop. Biocides are available to treat diesel fuels suspected of having microbial growth. The biocides are chemicals that kill bacteria and molds growing in fuel tanks without interfering with the combustion of the fuel or the operation of the engine. Used in very dilute concentrations, biocides can inhibit the growth of microbes over long periods of time, but they do not remove the accumulated sediment. For practical reasons, the fuel is filtered and the fuel tanks are cleaned periodically under scheduled maintenances.

Low temperatures can cause the biodiesel to gel, but will quickly liquefy again as the ambient temperature rises. In cold weather (near or below freezing), fuel additives can be used to prevent gellation. A preliminary study was undertaken on four different commercially available biodiesel additives on the low temperature behavior of biodiesel and blends (Biodiesel Tech Notes, University of Idaho 2005). The results of the study show that the additives have no effect on the cloud point temperature, but reduced the pour point temperatures. Future research is needed to investigate other additives to make biodiesel an all weather fuel.

Long-term storage of biodiesel under various environmental conditions is of interest. Biodiesel blends at 20 percent level with petroleum diesel have been shown to be stable at elevated temperatures and concentration of oxygen by NRL (Mushrush *et al.* 2000). Additional research studies are needed to determine effects of seawater on biodiesel blends, because some of the fuel Navy ship has taken on board in Europe contains about 5 percent mixture of biodiesel to DFM.

Emissions

All DoD ground combat vehicles are automatically exempt from emission controls under the 40 Code of Federal Regulations (CFR), 89.908. To meet the emission standards, vehicles would require a larger cooling system and engine to get the same performance. Fuel consumption would also increase as well as the thermal signature. The DoD has always made effort to meet emission standards as shown by a 90 percent reduction since 1980. However future standards would have drastic negative effects on DoD tactical vehicles without EPA waivers on a blanket basis for emission standards for year 2007 and beyond. The DoD could benefit in using biodiesel in their vehicles.

Biodiesel and blends with petroleum diesel have been shown to reduce smoke, soot, carbon monoxide and hydrocarbons. Biodiesel does not contain sulfur as found in petroleum diesel while the blends will have slightly lower content of sulfur. Sulfur results in sulfur dioxide emissions that cause acid rain and in the generation of sulfuric acid to corrode engine crank oil. Smoke and soot (particulate material of unburned fuel and carbon residues) are most visible pollutants from diesel engine exhaust. They can cause a wide range of health problems such as respiratory impairment. The combustion of biodiesel will not give off soot and smoke because the oxygenation in the biodiesel promotes complete combustion.

In 1998 report from the Southwest Research Institute, oxygen was shown to be the driving mechanism for soot reduction in truck engines operating on various blends of biodiesel. The higher the oxygen contents of the biodiesel blend, the greater the reduction in soot emissions. Some of the particulate emissions were found not only from the fuel, but also from the lubrication oil. Tests performed using a Cummins B-5.9 test engine lead to this finding. The results were that about 22 percent of the particulate emissions were from unburned lubrication oil and independent of the B20 blend and B100 fuel used. Carbon soot, in contrast, made up over

50 percent of the particulate emissions and this carbon soot component was reduced by 20 percent with the B20 blend, and reduced with the B100 by 66 percent in the Cummins B5.9 engine and by 71 percent with the Detroit Diesel engine.

Carbon monoxide emission is also reduced because the oxygenation in the biodiesel, which converts the carbon monoxide to carbon dioxide. In the 1998 report by the Southwest Research Institute, the levels of carbon monoxide were shown to be reduced from 8 to 22 percent with a B20 blend, depending on the type of engine. When the fuel was switched from low-sulfur petroleum diesel to B100, there was a 28 percent to 37 percent drop in the carbon monoxide emissions.

Polyaromatic hydrocarbons (PAHs) are a class of heavy oil petroleum defined by their multiple benzene ring structures. Their complex ring structures make them insoluble, slow to burn and carcinogenic. PAH emissions are regulated by the EPA. In the Southwest Research Institute report, the Cummins N-14 engine had a 12 percent decrease in PAH emissions when operating on B20 blend relative to petroleum diesel, and a 74 percent decrease in PAH emissions when using B100. The Detroit Diesel engine had a 29 percent reduction in PAH emissions operating on B20 blend and a 68 percent reduction when operating on B100. The data suggest major gains in improving the air quality around diesel engines in vehicles and boats operating on biodiesel.

Nitrogen oxide emissions are the result from the oxidation of atmospheric nitrogen at high temperatures inside the combustion chamber of the engine, rather than from the fuel. Nitrogen oxide emissions are considered a major contributor to ozone formation and by product of internal combustion engines. Several reports have shown that there is slight increase in nitrogen oxide emissions (seven percent) with biodiesel and blends, which were attributed to the higher oxygen content of the fuel mixture. Greater oxygen content in the fuel leads to better combustion of the fuel and more nitrogen oxide generation with biodiesel fuels. Some reduction in nitrogen oxide emissions could be obtained by retarding the timing of ignition and slow the burn rate of the fuel in the combustion chamber. However, this improvement was offset by the increases in hydrocarbon, carbon monoxide and soot and smoke emissions by the timing adjustment.

Producing and burning biodiesel creates a lower gain in CO_2 than petroleum diesel. Biofuels are produced from renewable agricultural crops that assimilate carbon dioxide from the atmosphere to become plants and vegetable oil. The carbon dioxide released this year from burning biofuels will be recaptured by next year crops. The combustion of petroleum fuel will always increase the concentration of carbon dioxide in the atmosphere. The U.S. is under considerable pressure from the international community (the December 1997 Kyoto Conference) to take seriously its efforts to reduce carbon dioxide, carbon monoxide and other greenhouse gases released, in part, by the combustion of fossil fuels in vehicles. North America is the highest CO_2 emitting region of the world with 1.82 billion tons of carbon in 2004 (Global, Regional, and National CO_2 Emissions 2007). This 2004 total is an all-time high for North America and represents a 1.6 percent increase from 2003. Supplementing our dwindling petroleum fuel reserves with biomass-based fuels (biodiesel, for petroleum diesel; biomass-based alcohols or hydrogen for gasoline) helps reduce the accumulation of carbon dioxide.

Marine Environmental Impact

The Navy is mandated to limit the concentration of oily (petroleum and lubrication oil) wastewater from the ships in U.S. and foreign harbors. Biodiesel, if accidentally released in the environment, will be viewed as a pollutant. The 1997 ruling under the Clean Water Act, as amended by the Oil Pollution Act of 1990, biodiesel is considered "oil" like petroleum. Studies have shown that biodiesel has lower impact on the environment than petroleum diesel, which contains more toxic and more water-soluble aromatics. The environmental impact of biodiesel is an important issue to address.

Biodiesel methyl esters are actually quite insoluble in sea or fresh water, with a saturation concentration of 7 ppm (sea) and 14 ppm (fresh) at 17^{o}C, whereas petroleum diesel can partition aromatics into water in concentrations of hundreds of ppm. The dissolved phase of the biodiesel methyl esters was shown to breakdown by the biodegradation action of naturally occurring bacteria in bay water. The half-life for the biodegradation of the vegetable methyl esters in agitated bay water was less than 4 days at 17^{o}C, about twice as fast as petroleum diesel. Cometabolism was observed in the biodegradation of petroleum fuels as much as three times faster with biodiesel than as the sole carbon source (Zhang *et al.* 2006, Pasqualinoa *et al.* 2006). These results were obtained by performing controlled laboratory tests by measuring carbon dioxide evolution by certain bacteria. Bacteria readily metabolize biodiesel, a simple, straight carbon chain with two oxygen atoms. The petroleum diesel hydrocarbons are less biodegradable because, they lack oxygen atoms.

Even though biodiesel spills are less toxic than petroleum diesel, studies have shown that biodiesel can harm waterfowls, mammals, and fish by coating their bodies and causing death by hypothermia or illness. The toxicity levels were measured for biodiesel by determining the LC50 value (concentration required to kill fifty percent of the population) to algae, floating and submerge macrophytes, invertebrates, and aquatic microcosms (Birchall *et al.* 1995).

Identify gaps and issues

The continued growth in biodiesel production capacity (Bantz and Deaton 2006) will be affected by:

- Biomass oil feedstock availability
- Biomass/diesel and glycerol prices
- Government regulations and incentives

The feedstock demand has increased by about 20 percent a year and has so far been met. Projection studies have suggested that this rate could cause the global price of vegetable oil to rise significantly. This uncertainty in the future has industry worried and their plan is to have many of the new plants capable of using multi-feedstock. The multi-feedstock will be cheaper and of lower quality than the desired soy oil. This solution has risks also. The cheaper feedstock is used in other competing markets, which may mean the cost may go up as demand increases. The lower quality feedstocks require more processing equipment, leading to a larger capital investment in building the plant. The amount of glycerol co-product produced may decrease with the lower quality feedstocks and decrease the potential revenue stream. Glycerol can be sold in crude or refined form. Refined glycerol is more expensive to produce, but a more valuable commodity for use in production of hundreds of other products. The chemical industry has forecast the price for glycerol will drop as the biodiesel plants continue on the present growth rate. Government, federal and state, incentives have increased the profitability for both the biodiesel producers and distributors. The Commodity Credit Corporation provides feedstock rebates to biodiesel producers, and the Internal Revenue Service offers federal excise tax credits to fuel blenders. These government subsidies have been made possible by the persistent lobbyists, keeping the price of biodiesel comparable to petroleum diesel and helping this industry to flourish. Market-based advocates are continuously arguing for removal of these incentives, making the future uncertain.

High-payoff areas for S&T investment

Biodiesel blend B20 has been tested extensively in many diesel engines. The industrial users and the Navy are interested in utilizing blends of biodiesel above 20 percent up to and including pure biodiesel (B100). The American Society of Testing and Materials has approved a standard for pure biodiesel when used in blends at 20 percent or lower. This standard was developed in cooperation with the vehicle, engine, fuel injection equipment companies; petroleum diesel and biodiesel producers and distributors; and state and federal regulators and third parties through the ASTM standard development process. Due to concerns of the US engine and fuel injection equipment manufacturers regarding influence of biodiesel fuels on cold flow properties, material compatibility, maintenance intervals, fuel stability, biological growth, energy content, and emissions influence with higher concentration blends, the ASTM standard has only been approved for blends containing less than and equal to 20 percent biodiesel.

The S&T investments are cold flow properties, material compatibility, maintenance intervals, fuel stability, biological growth, and emissions influence with higher concentration blends of biodiesel. Another area of interest is that there are many properties that were not determined for biodiesel (Table 11) should be measured for comparison with JP5 and DFM. One of the major shortcomings of biodiesel is the lower energy content than petroleum diesel. This is attributed to the presence of oxygen atoms in the methyl ester molecule. An energy efficient, synthetic route is desired to convert vegetable oil to JP5 and DFM surrogates (Kirkpatrick, D., 2007).

S&T Areas for NSWCCD

The properties of biodiesel that are not covered by ASTM D6751 can be determined for comparison to the MILSPECS of JP5 and DFM. The low temperature flow property of biodiesel could be improved through the use of additives. A study on improving the low-temperature flow properties suggests reducing the cloud point temperature rather than the cold pour temperature (Dunn, R. O., *et al.* 1995, 1996). One additive that has not been used with biodiesel is butanol. Butanol is a fuel derived from a biomass and has a lower freezing point than biodiesel. By developing blends of butanol and biodiesel, the butanol may depress the freezing point of biodiesel and lead to low temperature flow property without adversely affecting other properties. This biofuel blend of butanol and biodiesel does not require the addition of petroleum diesel. The penalty of this particular blend is the lower energy content than the B20 and petroleum diesel.

Fuel stability and biological growth are two additional areas for further studies. Fuels can remain in storage typically for a year and often longer without the formation of solids and biological growth. Fuels on Navy ships should be fairly immiscible with seawater, because the fuel tanks are seawater compensated. DFM is fairly inert in seawater. The DFM with five percent of biodiesel may be susceptible to biodegradation. A study is warranted to determine the long-term stability of DFM/biodiesel blends.

Carderock and Philadelphia personnel with expertise in materials characterization, including chemical analysis on fuels and microbiology, are well-suited to carry out these studies.

Pyrolysis Fuel

In Brief

Pyrolysis fuels are typically produced in one-step reactions where biomass is heated under pressure in the absence of O_2, with or without water (Figure 5). Most efforts in pyrolysis have focused on using a readily-available (wet) organic waste stream to produce a useful and valuable material, increasing resource utilization and minimizing waste. In pyrolysis, organic materials are only partially broken down, in contrast with processes that rely on syngas (Figure 6). The polymeric organic material is broken down into monomeric components and some chemical rearrangements occur. Incidental gaseous products like methane, ethylene, acetylene, and syngas ($CO+H_2$) are also produced, which can be burned to heat the reaction. Organic material derived from woody materials has more phenolics and acids, and the liquid fuel is quite different from petroleum-derived fuel (Barth *et al.* 2000). Such a fuel is not a good candidate for replacing petroleum fuels. Process feed material composed of fatty animal waste (offal) produces a liquid fuel that is more petroleum-like, having less oxygen (Adebanjo *et al.* 2005, Adenike *et al.* 2005, Lemly 2006).

Since pyrolysis of fatty material can provide a fuel similar to the Fischer-Tropsch process (described below), most of the considerations described below for Fischer-Tropsch fuel would likely apply for pyrolysis fuels, if they become more available. 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).

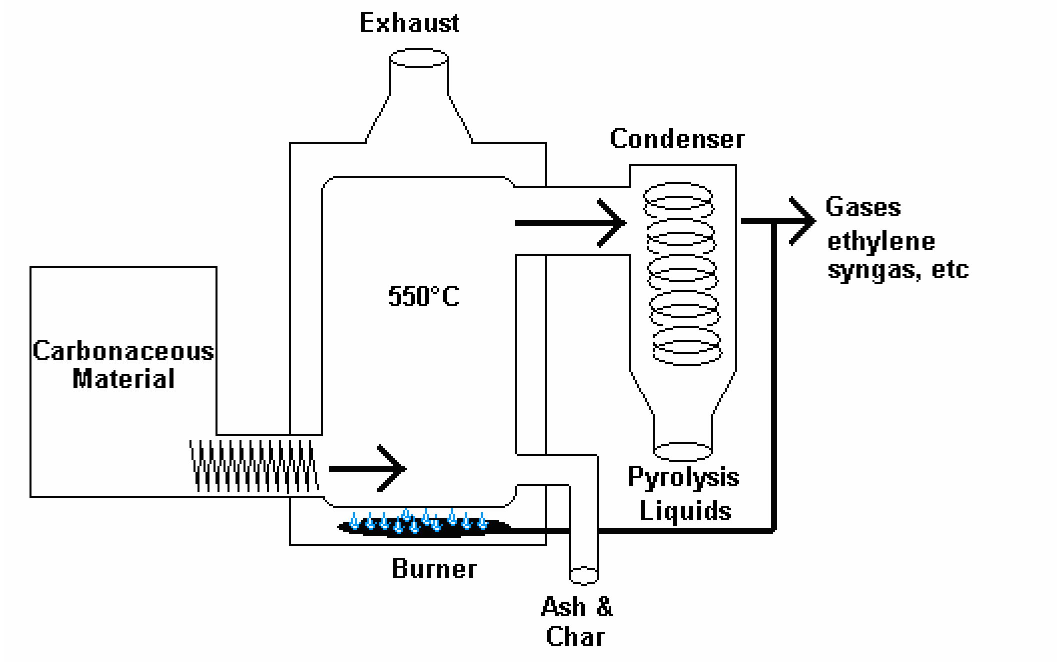


Figure 5. Schematic of pyrolysis to produce liquid fuels from biomass.

Fischer-Tropsch (F-T) Fuel

Sources and Production

F-T fuels are produced from carbonaceous material, *via* syngas ($H_2 + CO$) as an intermediate. Syngas is produced by hydrolysis (Figure 6) and/or partial oxidation of carbonaceous material (not shown) at higher temperatures than pyrolysis. 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 preferred feedstocks. The F-T process is similar to how methanol is produced (described previously), but requires different catalysts and longer reaction time. F-T reactions are multi-step, and require recycling of the syngas for several passes over the catalysts, but are simplified as:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O. \qquad \Delta h = -165 \text{ kJ/mol CO}$$

By modifying the reaction conditions, the F-T process can produce a variety of gaseous, liquid, and solid fuels. The specificity of the F-T process is not very high, except for the very low and the very high molecular weight products, like methane and heavy paraffin wax, respectively. Intermediate F-T liquid fuels have a range of molecular weights and chain branching, much like natural petroleum, but with more unsaturated hydrocarbons (olefins) and oxygenated compounds (5-15 percent alcohols, ketones, aldehydes, and acids), and fewer (often no) aromatics (Spath and Dayton 2003, Sliepcevich *et al.* 1977). The oxygen content of F-T fuel, in particular, may be a significant concern for the Navy. The effects of the differences between F-T and petroleum fuels are potential research topics (described below).

Using “clean coal” technology (described earlier), some portion of the gasified coal (syngas) could be diverted to a single-pass F-T process, such that the unreacted syngas can be burned in a turbine to generate electricity. The F-T process, being exothermic, can also contribute to the generation of steam for the combined cycle production of electricity. Such a process should be more efficient than a facility that only produces F-T fuel. A facility that efficiently produces both liquid transportation fuel and electricity from abundant domestic feedstocks (*i.e.* coal and waste organic material) is strategically valuable.

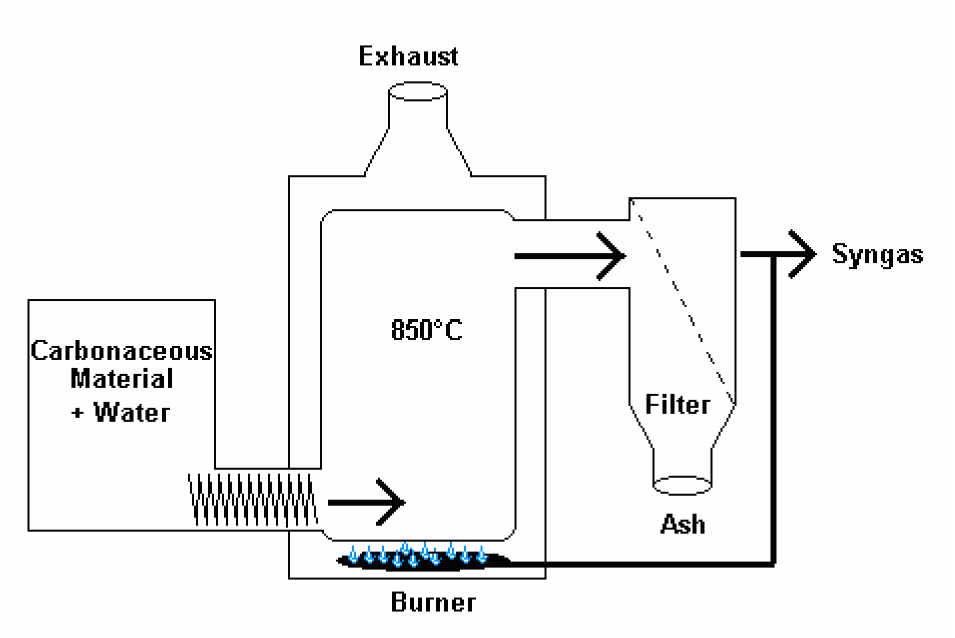


Figure 6. Schematic of syngas generation from organic material. The organic material is heated with water (steam) to high temperatures, where the organic material is hydrolyzed to syngas (CO + H_2). Some of the syngas is, or can be, burned to provide the necessary heat and steam.

Energy Balance

For every unit of fossil energy that goes into F-T fuel production, less than one unit of energy is available in the product. F-T fuels produced from coal have an energy balance of 0.4 (Sliepcevich *et al.* 1977). F-T fuel from natural gas is somewhat better, at 0.5. F-T fuels can be produced from biomass as well as from fossil fuel sources, however. Since biomass is produced with solar energy (in large part), to the extent that biomass can be used to produce syngas, the energy balance will increase and could be greater than 1.0 for an F-T plant using a 100 percent biomass feedstock.

Similarly, the carbon balance of the F-T process depends on the feedstock (Figure 7). With coal or natural gas as a feedstock, 2 or 2.5 times as much CO_2 is emitted relative to directly burning petroleum-derived fuel (Sichinga, 2006). Using coal as the feedstock for combined cycle electrical generation and F-T fuel synthesis, the overall efficiency is greater and the CO_2 impact is somewhat mitigated, being 1.5 times more than direct use of petroleum.

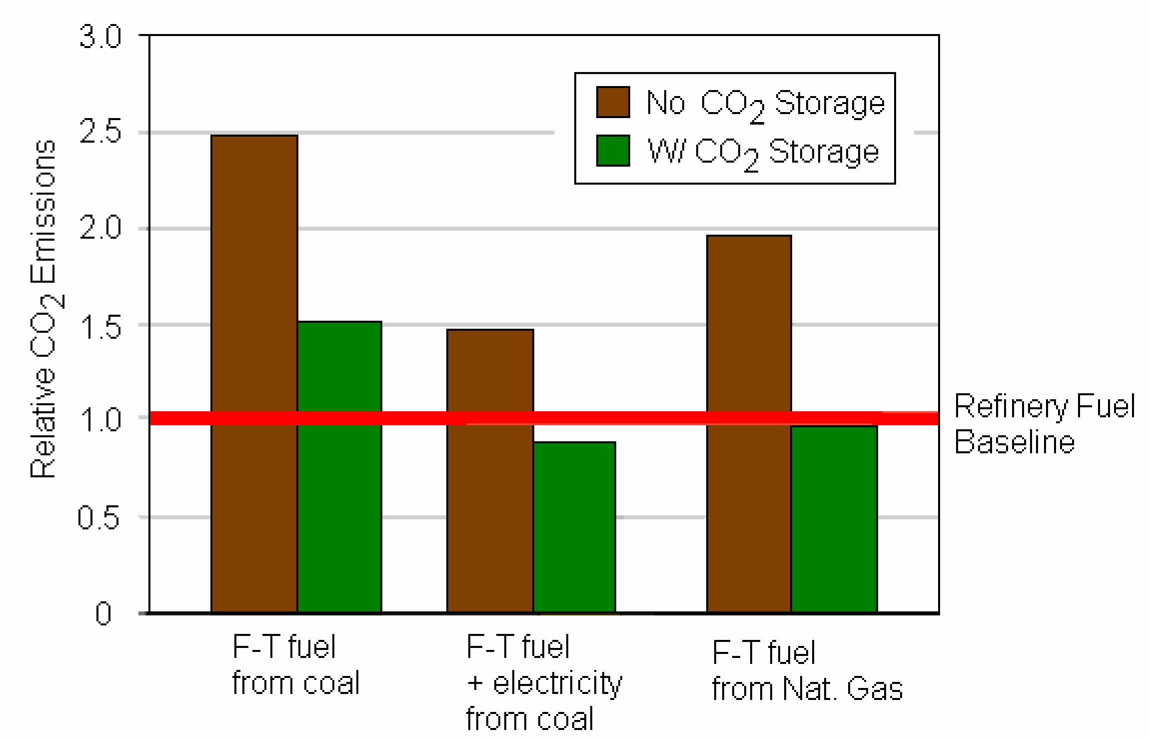


Figure 7. Relative CO_2 emissions from F-T processes fueled with coal or natural gas, with and without CO_2 sequestration. Baseline of "1.0" is relative to CO_2 emissions from petroleum derived fuel without any CO_2 sequestration. Adapted from Sichinga (2006).

With such a dramatic increase in CO_2 released, extensive production of liquid fuels by F-T processing of coal or natural gas would be environmentally ruinous in the absence of CO_2 sequestration. CO_2 sequestration increases the cost, however. The F-T process using biomass as the feedstock would release much less CO_2 than using petroleum (approaching zero), although no commercial plans for using biomass as feedstock could be located for this report. By combining CO_2 sequestration and use of biomass feedstock, the full strategic and environmental benefits of F-T fuel could be realized.

F-T as Fuel

F-T fuels were used extensively by Germany in World War II, and in South Africa from the 1950's. F-T fuels are inherently diesel-like and low in sulfur and aromatics content, and are generally usable, without further processing, in diesel engines. Upon combustion in diesel engines, F-T fuel produces lower concentrations of carbon monoxide, hydrocarbons, particulate matter, and nitrogen oxides in the exhaust, when compared to #2 diesel (Clark *et al.* 1999). The energy density of F-T fuel is similar to, or perhaps slightly less than petroleum fuels (Figure 1 and Table 2).

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 2007b). Consistent with this goal, as part of the "Assured Fuel Initiative" from the Office of the Secretary of Defense, the

U.S. Air Force has recently begun studying the use of a (JP-8-like) F-T fuel produced originally from natural gas (methane) with a B-52 Stratofortress as the test-bed (Woodbury 2006, DESC 2007a). The fuel is produced by the Syntroleum Corporation. Tests prior to 2007 have included running four engines on 50 percent F-T fuel (balance JP-8) and running all eight engines on 50 percent F-T fuel. Based on these tests, the B-52 has been certified to fly using 50 percent F-T fuel. The Air Force plans to have every airframe certified to fly on this 50 percent blend by 2011 (Hernandez 2007). These Air Force tests should be relevant to any Navy applications, although the particular storage and transport requirements of the Navy would require additional testing.

Economic and Technological Gaps

Although the F-T process has not been widely commercialized, the technology is fairly mature, having seen use by Germany and Japan in World War II and South Africa up to the present (Sliepcevich *et al.* 1977, Bergeron *et al.* 2007). 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 because during the apartheid era, it was politically difficult for them to import enough petroleum. Thus, in these cases, the political situation favored F-T derived fuel, even though it was more expensive.

Certain improvements are likely to be realized as the F-T process comes into wider use, although there are no major technological gaps. Chevron, Choren, Shell Oil, and Sasol are involved in various F-T projects in Indonesia, China, Qatar, and the U.S.A. (Bergeron *et al.* 2007). Sasol, with its long experience in South Africa, is the world leader in F-T technology. Extensive commercialization of the F-T process should include considerations for CO_2 sequestration. There are a number of technological and logistical problems when CO_2 sequestration is considered along with F-T fuel production (Martinez-Frias *et al.* 2003). These issues, however important, are beyond the scope of this report.

High petroleum prices favor increased use and investments in all alternatives, including F-T fuel. Thus, barriers to widespread commercialization of the F-T have more to do with economic, rather than technological issues. The Defense Energy Support Center has established that potential 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 economic feasibility of F-T fuel is primarily dependant on the price of petroleum (Sichinga 2006).

Potential for Carderock Division in Fischer-Tropsch and Pyrolysis Fuels Research, Development, Testing, and Evaluation (RDT&E)

Although F-T and pyrolysis fuels are similar to petroleum fuels, the differences are important with regards to the needs of the U.S. Navy. The differences in hydrocarbon saturation and oxygenation may cause significant problems. Basic, experiment-based research on how these differences will affect the fuel stability is appropriate for the involvement of Carderock Division personnel.

The hydrocarbon saturation level is related to fuel stability. Carbon-carbon double bonds in olefins tend to form crosslinks between chains, leading to varnish and sludge. As already mentioned, DFM is specified as a distillate fuel to avoid the olefin content of reformed (cracked) fuel. F-T fuel may not be able to meet this requirement. Addressing this possible deficiency in F-T fuel may be as simple as an additive that inhibits crosslinking, however.

The issue of oxygenated compounds in fuel is two-fold. Firstly, oxygenated compounds will tend to be more soluble in seawater, would increase the solubility of seawater in fuel, and would tend to favor the formation of seawater/fuel emulsions. Secondly oxygenated hydrocarbons tend to be more easily biodegradable than regular hydrocarbons and could stimulate more and/or faster bacterial growth. The issue of emulsions could greatly affect the suitability of F-T fuel for Navy use.

Oxygenated compounds are more biodegradable both because of higher aqueous solubility and because heteroatoms like oxygen, in what would otherwise be a purely hydrocarbon, serve to biochemically "activate" the molecule (Berry *et al.* 1987). The first step in oxidation of hydrocarbons is adding oxygen (Van Hamme *et al.* 2003). As the bacteria that degrade hydrocarbons grow, they also produce emulsifiers to increase the hydrocarbon bioavailability. As long as molecular oxygen is available (O_2, dissolved in seawater), biodegradation of a synthetic fuel might be more problematic than its petroleum counterpart.

Thus, it is likely that F-T fuels would behave differently than petroleum fuels, given the particular storage requirements of the Navy. The issue of seawater-compensated fuel storage may be particularly critical to the suitability of F-T fuel as a petroleum fuel replacement. The chemical and biochemical stability of any alternative fuel under Navy-relevant conditions must be experimentally determined.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS FOR FURTHER WORK

Several alternative fuels, in use or being considered for use in the commercial sector, were evaluated for their suitability for Navy use. The alcohol fuels methanol, ethanol, and butanol were found to be generally unsuitable for Navy tactical use. Ethanol blends with gasoline are currently used in non-tactical vehicles. Methanol and butanol are also suitable for non-tactical use. Butanol has numerous properties that make it attractive as a potential additive to gasoline or commercial diesel fuel for use in non-tactical vehicles. Biodiesel is currently being used in non-tactical vehicles and biodiesel blends may be considered for tactical use. Biodiesel fuels may have limited tactical use because of their lower energy density.

Of the several alternative fuels under our consideration, only Fisher-Tropsch (F-T) and pyrolysis fuels are likely to be suitable replacements for petroleum fuels in tactical vehicles. F-T and pyrolysis fuels are the most similar to petroleum fuels, with regard to energy density, solubility in water, and flash point. These are the most critical parameters for Navy tactical use.

The bulk properties of F-T and pyrolysis fuels can be manufactured to be similar to Navy petroleum distillates. However, many of the explicitly specified properties as well as additional implicit properties may be sufficiently different from Navy fuels that their use may be problematic for the Navy. Navy tactical fuels have different specifications than those of the other armed forces, such that experimentation with alternative fuels for Navy use must be performed with those particular specifications in mind. The Navy cannot rely on the evaluations of alternative fuels to be used by the other services. It will need to test, evaluate, and specify fuels that meet the Navy's unique requirements.

The recommendations for expanding S&T knowledge base are the following:

1. Develop MILSPEC type standards for F-T fuels, butanol blends, and biodiesel blends with petroleum fuels.
2. Determine the long-term chemical and biochemical stabilities in contact with seawater for the above fuels.
3. Evaluate and develop strategies for mitigating particular properties of concern for alternative fuels, such as low temperature flow properties of biodiesel.
4. Characterize the synthetic fuels that are developed under the Biofuels Program of DARPA.

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