

BACKGROUND: BIODIESEL AND OTHER BIOFUELS¹

Biofuels are renewable fuel sources that are increasingly being considered as blending components or replacement for traditional petroleum fuels, primarily for use in internal combustion engines and heating appliances. Environmental, economic and geopolitical factors have created a market for the biofuels methanol, ethanol, butanol and biodiesel. They are being initially introduced as low blend percentages for use in engines and appliances designed for traditional fuels. As an expanding market, biofuel usage is expected to significantly increase as production capacity is brought on line and additional market incentives are made available.

This Fact Finding Investigation is focused on “B5 biodiesel blends²”. For reasons outlined elsewhere in this report, the 5 percent biodiesel blend is being compared to No. 2 fuel oil when used in residential oil heating appliances to identify performance and/or compatibility issues.

“Biodiesel” and “biofuels” are terms that are loosely used in the popular media. Therefore, the first step in this investigation was to define and describe what bioheat was, and what the appropriate components for blending were. The base petroleum fuel (No. 2 fuel oil) had been previously defined, and has been used for many years. However, the blend stock is specified on a performance-related property basis that is not prescriptive of the base stock. As with any other naturally occurring or naturally originated material, there is a range of properties to consider for the biodiesel blend stock. For the purposes of this investigation, it was therefore necessary to consider the fuel feedstock, processing variations and differences in chemical composition that could impact results.

For biodiesel blends, UL is assessing potential safety aspects, developing test procedures, and establishing guidelines. As part of this effort UL seeks to understand relevant property and performance differences with conventional fuels. This background section provides a summary of this UL effort and describes the resulting fuel composition set for use in test procedures.

Biodiesel Chemistry

“Biodiesel” is defined in ASTM D6751 as “a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100” and is otherwise generally known as fatty acid methyl esters (FAME). In simple chemical terms, biodiesel is a long chain fatty acid ester composed of a short chain alcohol (i.e., methanol) and a long chain fatty acid. Fats and vegetable oils are esters of long-chain fatty acids and glycerol (a molecule containing three functional alcohol groups). Fatty acids may be either saturated or unsaturated; that is, the long hydrocarbon chains that possess single (saturated) and/or double (unsaturated) covalent bonds. The term “saturation” refers to the ratio of carbon to hydrogen and the term “unsaturation” indicates that the carbon atoms do not have the maximum possible amount of hydrogen present. These functional differences relate to fuel feedstock and affect fuel processing and are important when selecting representative test fuels. They also dictate physical and chemical properties of the fuels and may affect chemical stability and performance over time.

¹ The information in this section was drawn mainly from publicly available sources. In addition to those specifically cited in the narrative, the following documents served as principle sources; *Biodiesel Handling and Use Guidelines – US Department of Energy & National Renewable Energy Lab*, *SAE J1681 Recommended Practice for Gasoline, Alcohol and Diesel Fuel Surrogates for Materials Tests*, and *ASTM D6496-04 Standard Guide for Microbial Contamination in Fuels and Fuel Systems, Organic Chemistry*, J. B. Hendricks, D. J. Cram and G. S. Hammond, *Petroleum Geology and Geochemistry*, J. M. Hunt.

² When referred to in this Report, “B5 biodiesel blend” is comprised of five percent by volume ASTM D6751 (Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels) and ninety five percent ASTM D396 (Standard Specification for Fuel Oils) No. 2 fuel oil. Note: for the purposes of this Report, “B5 biodiesel blend” and “UL B5 biodiesel blend” are two distinct fuels.

Biodiesel feedstocks are derived from three general organic sources: 1) vegetable oils (soy, corn, canola, rapeseed, sunflower, cottonseed, etc.) and tropical oils (palm, coconut, olive, etc.), 2) animal fats (yellow grease, white grease, beef tallow, chicken fat, fish oils, etc.) and 3) recycled fats & oils (any combination of the above from commercial restaurants and processing plants).

These fats and oils are commonly known as triglycerides; that is, chemical compounds with a three carbon-glycerin backbone to which individual fatty acids are covalently attached by ester linkages. Each bio-based feedstock is also composed of a mixture of different fatty acid carbon chain lengths that range from 12-22 carbons for the ten most common types but, of these, 90% have 16-18 carbons.

Biodiesel is produced through a reactive chemical process called transesterification. This process consists of reacting bio (oil or fat) feedstocks with short chain alcohols (typically methanol) and a catalyst (typically sodium or potassium hydroxide). In essence, the triglyceride ester is broken into glycerol and three alkyl esters by substituting three mono-functional alcohol molecules for the tri-functional glycerol. The biodiesel is refined by washing and filtration to remove excess unreacted alcohol, catalyst, and glycerol. A specification, ASTM D6751, exists for the purity and quality of the biodiesel product. As with petroleum-based fuels, biomass-based fuels have many sources and process variations. Biofuels are therefore typically batch manufactured to compensate for chemical variation and ensure consistent quality end fuel.

Fuel Composition

The introduction of biodiesel into the supply chain (production, distribution and consumption) can impact a number of factors such as fire, combustion, material compatibility and contamination. This impact can be assessed by comparing the physical and chemical (molecular) properties of petroleum and biomass fuels.

A basic comparison of the properties of No. 2 fuel oil and B100 biodiesel are provided below in Table 1

As a result of the higher flash point, B100 biodiesel is considered less of a fire risk than No. 2 fuel oil, but potentially could have low temperature operational issues due to the solidifying point of saturated fatty acids, process by-products or other organic contaminants. B100 biodiesel has some additional unique chemical differences arising from the ester functionality: a) higher electrical conductivity (4-5X), b) increased moisture sensitivity (approx 10X), c) increased polarity and solvency (due to the ester dipole moment), d) chemical reactivity (hydrolysis of the ester and reactivity of functional groups that may be present) and e) microbial sensitivity (metabolism of the ester fatty acids). Although B100 biodiesel is a minor component in the blended (B5 biodiesel blend) fuel makeup, understanding and evaluating how they would impact the performance of oil heating equipment is critical, even at low blends. Regarding the solvency question, according to Brookhaven National Laboratories a recent study has shown B100 does not have a measurable solvent behavior toward sludge deposits commonly found at the bottom of home heating storage tanks. The solubility limit of water in B100 biodiesel is 1000-1800 ppm as compared with petroleum fuel, which is 50-150 ppm. Both of these levels are considered very low. Temperature swings and contamination with physical and biological agents play a significant role in the process of acquiring and separating water from the fuel, which is also the case with petroleum fuels

Table 1³
Comparison of Typical Fuel Properties, No. 2 Heating Oil and Biodiesel

Property	No. 2 Heating Oil	Biodiesel (B100)
Standard	ASTM D396	ASTM D6751
Higher Heating Value (Btu/gal)	139,200	125,000
Kinematic viscosity (@ 40 F)	2.7	4.0 – 6.0
Specific gravity (kg/liter @ 60 F)	0.86	0.88
Density (lb/gal)	7.1	7.25
Water and Sediment (vol %)	0.001	0.05
Carbon (wt %)	86.6	77.0
Hydrogen (wt %)	13.6	12.0
Oxygen (wt %)	0.1	11.0
Sulfur (wt %)	0.1	0.0 – 0.0024
Flash Point (F)	120 – 210	210 - 350
Cloud Point (F)	-13 – 14	26 – 54
Pour Point (F)	-22 – 5	5 – 50

³ Table 1 was generated from the following sources:

Baukal, C. E., and Schwartz, R., The John Zink Combustion Handbook CRC Press, 2001.

Stultz, S.C. and Kitto, J.B., Steam, Its Generation and Use, Babcock and Wilcox, 1992.

C-E Fuel Burning and Steam Generating Handbook, Combustion Engineering, Inc., 1973.

ASHRAE Handbook of Fundamentals, 2005

American Society of Heating, Refrigeration, and Air Conditioning Engineers, 2005.

Northrop Grumman, TRW, and NIPER, Heating Oils, 1998 through Heating Oils, 2006.

BDM Petroleum Technologies, TRW Petroleum Technologies, Northrop Grumman, 1998 through 2006.

Contamination

All fuels are susceptible to contamination at various points along the supply chain from the production (unrecovered processing residuals), transport (unclean pipes and vessels), storage (tank openings) and fuel aging and degradation. These contamination points primarily introduce water, “color-bodies” (short length polymers of the fuel molecules), salts, organic and inorganic acids and microbes into the fuels that may cause them to shift out of specification and negatively affect material compatibility and system performance. It is realized that these contaminants cannot be completely controlled, especially in residential heating systems that potentially are not inspected or maintained by homeowners.

Water contaminants are not uncommon in residential oil tanks from supply chain contamination or atmospheric condensation as the fuel level in the tank is lowered and displaced with outside air. Biodiesel is somewhat hygroscopic which may contribute to water contamination and possible water separation if the total water exceeds a level of 0.1%, which is only slightly higher than petroleum fuels. Salts may be introduced from salt air aerosols. Acids may come from residual process compounds during refining, ester hydrolysis, or microbial growth byproducts. ASTM fuel specifications for water limits do not address the postproduction environment, however they are of concern to the operation of heating oil equipment.

Microbes enter fuel from various terrestrial or atmospheric sources and may colonize water/fuel interfaces. Biodiesel may be more susceptible to microbial growth (fatty ester metabolism) as it is more hygroscopic and less toxic. Ester hydrolysis leads to the formation of free acids and alcohols, which accounts for the increased moisture sensitivity over time. The microbes may metabolize the hydrocarbon chains in water that migrates to the storage tank bottom, in thin films in phase separation or even top surface condensation. Residential heating fuels may have even higher potential for contamination from microbial flora in the tank due to the warmer, undisturbed breeding environment in the non-heating-season

Fuel decomposition is a natural consequence of microbial activity, hydrolysis, oxidation, heating or other chemical processes and can often be seen in the production of color bodies that darken the fuel. Biodiesel decomposition increases acidity (souring). It is currently unknown if the recent addition of a fuel stability minimum to the ASTM D6751 specification will mitigate this. However, it is likely that heating oil blends because of long storage times may be susceptible to fuel decomposition, and thus a B5 biodiesel blend may have an impact on appropriate storage life, but again, residential heating fuels are at increased risk due to long dormant off season periods.

General Material Compatibility

Significant research has been done on biodiesel compatibility with products and materials relative to diesel engines. This may or may not be entirely transferable to parts of residential heating equipment in direct contact with fuels. However, broad compatibility conclusions from diesel engine applications are instructive for basic engineering materials in common with heating equipment.

B100 biodiesel does not exhibit long-term compatibility with: a) certain soft metals (copper, brass, bronze, lead, tin and zinc), b) polymers (polyethylene, polypropylene), and c) elastomers (among them, buna-n, nitrile and non-oil resistant rubbers). Conversely, harder metals (steel), many, but not all fiber reinforced plastics (FRP's), nylons, fluoropolymers and fluoroelastomers generally exhibit greater chemical resistance⁴. Assurance of material compatibility with biodiesel blends should be verified on a case-by-case basis to ensure long-term performance. The individual components and combination(s) of components in residential heating systems add complexity, especially where they differ from the diesel engine systems studied.

⁴ Many automotive research projects have been undertaken to determine the effects of biodiesel on the physical properties of polymeric materials in fuel conveying systems, such as gaskets, seals, o-rings, etc. One study looked at the particular effects introducing soy-based biodiesel blends (20-100%) into systems designed for petroleum fuel (diesel, fuel oils) can have on metals and elastomers. For details, reference should be made to *Compatibility of Elastomers and Metals in Biodiesel Fuel Blends*, Gary B. Bessee, Joseph P. Fey, Southwest Research Institute, 1997. ©Society of Automotive Engineers, Inc.

Long-term material compatibility with fuels is typically concerned with retention of physical properties and resistance to material migration that may result in contamination of the fuel. Metallic corrosion and nonmetallic degradation are accelerated by fuel contamination or 'out of specification' fuel (described previously). Again, dormant residential heating systems may present increased risk.

For metals, there are a number of different corrosion mechanisms that can occur, however there are at least two that are significant to biodiesel: galvanic and pitting corrosion. Galvanic corrosion is driven by the electrochemical potential of dissimilar metals in the presence of conducting fluids. The hygroscopic susceptibility of biodiesel (moisture uptake), ester polarity and the presence of soluble ionic contaminants increase the conductivity of the fuel. The higher concentration of trace minerals, salts and acids, individually or in combination, will accelerate corrosion by attacking protective oxide films and / or increasing conductivity that promotes galvanic action more easily than fuel oil. Pitting corrosion occurs when there is localized damage to the protective oxide film that is exacerbated by ionic or conductive fluids in contact with the metal surfaces.

For non-metals (thermosets, thermoplastics and elastomers), the ester-based biofuels may initiate change by solvating and penetrating (i.e., swelling) the material followed by possible extraction (especially low molecular weight plasticizers and/or stabilizers and additives). The polarity of biodiesel increases its solvency and facilitates permeation and extraction. Solvation, swelling and/or extraction leads to changes in key physical properties of materials such as modulus, tensile strength, elongation, flexibility, impact and dimensional change. These changes, in turn, could lead to further permeation. Extraction alters the fuel chemistry and could increase degradation potential for other parts further along the fuel train. The chemical changes noted above could also accelerate degradation (hydrolysis, oxidation) of the material with the loss of additives and stabilizers.

Metallic corrosion and polymer degradation could potentially result in altered performance of equipment and could result in suspended solids in the system. The extent of the degradation, and the size of the particulates could affect the performance of filters and nozzles.

The physical and/or chemical changes noted above for metals and nonmetals could lead to malfunction, leakage or even failure of individual components in the system.

Representative Test Fuels

The compositional differences between biofuels may significantly affect material compatibility and equipment performance. For this investigation, the test fuels, along with key hydrocarbon components were selected to simulate "worst case" fuel conditions. That is, the properties exhibited by this representative test fuel composition could be achieved under certain realistic conditions in the field. This was the rationale for recent development and use of "aggressive" fuels by various SAE and UL technical committees that focus on evaluation of fuel containing or consuming products. The "UL B5⁵ biodiesel blend" test fuel described in this Fact Finding Investigation was blended from UL B100 biodiesel stock, developed as described below.

This synthetic test fuel is considered more aggressive than B5 blend biodiesel because of the increased acidity and moisture content of the UL B100 biodiesel stock. Therefore, "UL B5 biodiesel blend" was utilized for selected material capability and endurance testing. For combustion and other testing, the standard B5 biodiesel blend, as defined by this Report, was considered sufficient.

Major fuel components include alkanes (aliphatics or paraffins), aromatics (naphthenes or naphthene aromatics), oxygenates (any molecule containing covalent oxygen) and additives (detergents, stabilizers, colorants, etc.). With respect to domestic heating systems fuels, petroleum hydrocarbons are divided between the alkane and aromatic fractions, and biodiesel represents the oxygenates (esters). Additives have typically not been included in test fuels, as they are in trace amounts and industry has not agreed on representative generic chemical additives.

⁵ When referred to in this Report, "UL B5 biodiesel blend" is comprised of five percent by volume UL B100 and ninety five percent ASTM D396 (Standard Specification for Fuel Oils) No. 2 fuel oil.

Major fuel contaminants include water (arising from hygroscopic biofuels and external contamination), salts (typically sodium chloride), organic acids (arising from production, hydrolysis or microbial activity), inorganic acids (mineral acids, such as hydrochloric or sulfuric) and peroxides (arising from the reaction of oxygen with unsaturated compounds). With respect to the test fuels developed, such as UL B100 biodiesel, all these contaminants are reflected in the synthetic composition except for peroxides (there is no technical agreement on the amount or type yet). Sulfur compounds are represented in the base fuels and therefore considered represented.

The UL Standards Technical Panel (STP) responsible for the *Standard for Nonmetallic Underground Piping for Flammable Liquids*, UL 971, developed the UL B100 biodiesel test fuel formula. That STP convened specialized Work Groups, consisting of UL and industry experts, for the purpose of developing requirements for the containment of flammable liquids. Findings relevant to this Fact Finding investigation include the following.

- A 99.8% soy feedstock was selected as a worst case representative of all feedstock as it combined balanced composition percentages and low fuel stability.
- It was determined that the biodiesel chain length and saturation level were not as significant as the aggressive components in evaluating material compatibility. Therefore, a mixture of 0.2% acid water (decanoic acid and DI water) was used with Acid Number adjustment (additional biodiesel or decanoic acid to the final mix to reach a consistent 1.0% +/- 0.02).
- The water volume was tied to saturation levels in biodiesel, decanoic acid represented biodiesel decay byproducts and the Acid Number, based on the D6751 specification of max 0.5, is a 2-times (2x) safety factor.

Therefore, the final fuel component makeup of the B5 biodiesel blend test fuel used in this investigation consisted of approximately 95% petroleum, 5% oxygenate and trace aggressive salts and acids. Note that the addition of salt and, in some instances, deference to automotive fuel was not considered to invalidate the B5 biodiesel blend test fuel for residential heating equipment. However, the impact of these variables should be considered if future testing at higher blends is conducted with the test fuel.