# Biodiesel Use in Underground Metal and Non-metal Mines

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## INTRODUCTION

Biodiesel is not a new fuel to North America. In fact, activities date back to the late 70's and early 80's. As a result of the OPEC crisis, a significant amount of research on biodiesel and other domestically produced fuel was conducted by various universities and government agencies. The general conclusion at that time was that biodiesel was a technically acceptable substitute, replacement, or blending stock for conventional petroleum diesel, but that its costs were prohibitive compared to petroleum based diesel fuel. Concern over the health impacts of diesel fuel exhaust and proposed regulations has spurred the recent activities to commercialize biodiesel in North America and opened doors for its use in confined areas such as underground mines.

## WHAT IS BIODIESEL?

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol in the presence of a catalyst to yield glycerin and biodiesel (chemically called methyl esters). Biodiesel has been registered with the US Environmental Protection Agency as a pure fuel or as a fuel additive and is a legal fuel for commerce. Biodiesel is an alternative fuel which can be used in neat form, or blended with petroleum diesel for use in compression ignition (diesel) engines. Its physical and chemical properties as it relates to operation of diesel engines are similar to petroleum based diesel fuel. The specification for pure (100%) biodiesel is described in Table 1† and is in the process of being approved by ASTM.

Table 1. Biodiesel Specifications (as of July, 1996).

| **Property** | **ASTM Method** | **Value** | **Unit** |
|---|---|---|---|
| Flash Point | D93 | 100.0 min. | °C |
| Water & Sediment | D1796 | 0.050 max. | vol. % |
| Carbon Residue (100 % sample) | D4530‡ | 0.050 max. | wt % |
| Sulfated Ash | D874 | 0.020 max. | wt % |
| Viscosity @ 40°C | D445 | 1.9 - 6.5 | Cst |
| Sulfur | D2622 | 0.05 max. | wt % |
| Cetane Number | D613 | 40 min. | |
| Cloud Point | D2500 | by customer | °C |
| Copper Strip Corrosion | D130 | No. 3b max. | |
| Acid Number | D664 | 0.80 max. | mg KOH/gm |
| Free Glycerin | G.C.§ | 0.020 max. | wt % |

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| | | | |
|---|---|---|---|
| Total Glycerin | G.C.§ | 0.240 max. | wt % |

† *This specification is in the process of being evaluated by ASTM. A considerable amount of experience exists in the US with a 20% blend of biodiesel with 80% petroleum based diesel. Although biodiesel can be used in the pure form, use of blends of over 20% biodiesel should be evaluated on a case by case basis until further experience is available.*

‡ *Or equivalent ASTM testing method.*

§ *Austrian (Christiana Planc) update of USDA test method.*

# BIODIESEL ATTRIBUTES

*Emissions Reductions*

The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle and testing methods. Particulate emissions, the focus of DEEP, from conventional diesel engines can be divided into three components. Each component is present in varying degrees depending on fuel properties, engine design and operating parameters.

The first component, and the one most closely related to the visible smoke often associated with diesel exhaust, is the carbonanceous material. This material is in the form of sub-micron sized carbon particles which are formed during the diesel combustion process and is especially prevalent under conditions when the fuel-air ratio is overly rich. This can occur as a result of insufficient combustion air, overfueling or poor in-cylinder fuel-air mixing. The second component is hydrocarbon or PAH material which is absorbed on the carbon particles. A portion of this material is the result of incomplete combustion of the fuel, and the remainder is derived from the engine lube oil. Finally, the third particulate component is comprised of sulfates and bound water. The amount of this material is directly related to the fuel sulfur content.

The use of biodiesel decreases the solid carbon fraction of particulate matter, eliminates the sulfate fraction (as there is no sulfur in the fuel), while the soluble, or hydrocarbon, fraction stays the same or is increased. Therefore, biodiesel works well with new technologies such as catalysts (which reduces the soluble fraction of diesel particulate), particulate traps, and exhaust gas recirculation (potentially longer engine life due to less carbon).

Biodiesel's particulate reduction has been verified in both lab and field testing completed by the former US Bureau of Mines (USBOM). Lab testing was conducted with a power pack from a Jeffrey 4110 RamCar powered by a Deutz/MWM 6.3 liter naturally aspirated IDI engine with a water scrubber. The test was performed both with and without a prototype diesel oxidation catalyst. Particulate matter reductions of 50% were obtained when using neat biodiesel compared to diesel fuel. The addition of the catalyst reduced the biodiesel SOF by an additional 48%. In this test, the addition of a catalyst to the diesel fueled engine increased DPM due to sulfate aerosol formation.

The USBOM conducted field tests at Homestake Mines in South Dakota and measured both energy specific DPM using ambient air samplers as well as time weighted DPM on samplers attached to the equipment itself. These results demonstrated an energy specific DPM reduction of 75% and a time weighted DPM reduction of 55%. These reductions were greater than that of the laboratory, most likely due to the heavier duty cycle used in the mine compared to that used in the lab testing. Equipment operators also commented on the distinct absence of black smoke upon acceleration when using biodiesel.

*Operating Performance*

One of the major advantages of biodiesel is the fact that it can be used in existing engines and fuel injection equipment without negative impacts to operating performance. Biodiesel has a higher cetane number than conventional diesel fuel and its demonstrated use at the Homestake mine in South Dakota resulted in similar fuel consumption, horsepower, torque, and haulage rates compared to conventional diesel fuel.

*Health Effects*

Evidence does exist which indicates that diesel particulate matter is a potential carcinogen. In 1988, the National Institute for Occupational Safety and Health (NIOSH) recommended that whole diesel exhaust be regarded as "a potential occupational carcinogen, " as defined in the Cancer Policy of the Occupational Safety and Health Administration. The use of biodiesel does result in decreases in most regulated emissions. Relative to health effects, research results indicate that particulate matter, specifically the carbon or insoluble fraction, is significantly reduced. In addition to reducing the overall levels of pollutants and carbon, the compounds that are prevalent in biodiesel and diesel fuel exhaust are different. Preliminary research on the speciation of diesel and biodiesel particulate indicates that biodiesel exhaust has less harmful impacts on human health than petrodiesel.

The USBOM has also completed Ames mutagenicity testing of the DPM and exhaust gases from engines fueled with biodiesel to better understand how the use of biodiesel may impact the health of miners. Samples were taken from the exhaust of a Caterpillar 3304 PCNA equipped with an exhaust catalyst. Test results documented that the use of biodiesel reduced the Ames mutagenicity of DPM by 50% over conventional diesel fuel. In addition, the gas phase mutagenicity of biodiesel was negligible. USBOM researchers believed the strong reduction in mutagenicity may be due to the lack of aromatics or polycyclic aromatic hydrocarbons (PAHs) in the biodiesel fuel and, subsequently, in the exhaust gases. Tests from Europe confirm the reduction in DPM PAH using biodiesel blends as outlined below:

Table 2. Gaseous PAH levels of diesel fuel and a 50% biodiesel blend.

| | Diesel | 50% Biodiesel |
|---|---|---|
| | —- *µg/cycle* --- | |
| Naphthalene | 331,654 | 384 |
| Methyl-2 Naphthalene | 10,289 | 329 |
| Fluorene | 1,864 | 368 |
| Anthracne | 4,301 | 873 |

*Lubricity*

With the lubricity of conventional diesel fuel being scrutinized due to processing changes required to reduce the sulfur and aromatic content of diesel fuel, biodiesel use can be demonstrated to be a benefit. Lubricity tests utilizing both the High Frequency Reciprocating Rig (HFRR) and the Ball

On Cylinder Lubricity Evaluator (BOCLE) have demonstrated the lubricity advantage of biodiesel. Test results are detailed below.

Table 3. Exxon lubricity results using the HFRR* test at 60° C.

| Fuel Type | Scar | Friction | Film % |
|---|---|---|---|
| #2 LSD (reference fuel) | 492 | 0.24 | 32 |
| B20 with reference fuel | 193 | 0.13 | 93 |
| 1000 ppm Exxon lubricity additive with reference fuel | 192 | 0.13 | 82 |

** Results Courtesy of Midwest Biofuels*

Tests have also been conducted on Jet A-1 fuel. These test results from Southwest Research Institute concluded that biodiesel shows significant lubricity improvement compared to diesel fuel. Results are detailed below.

Table 4. Effects of biodiesel on Jet A-1 lubricity as determined by the HFRR test*.

| Fuel | HFRR, mm |
|---|---|
| Biodiesel | 0.27 |
| Jet A-1 | 0.66 |
| Jet A-1 + 8 vol% biodiesel | 0.28 |
| Jet A-1 + 4 vol% biodiesel | 0.28 |
| Jet A-1 + 2 vol% biodiesel | 0.20 |
| Jet A-1 + 1 vol% biodiesel | 0.34 |

** Tests performed by Southwest Research Institute (SwRI) are not an endorsement of biodiesel by SwRI. Tests funded jointly by the USDA and the USDOD.*

### *Flash Point and Sulfur Content*

The flash point of a fuel is defined as the temperature to which the fuel must be heated to produce a vapor-air mixture above the surface of the fuel that will ignite when exposed to an ignition source such as a spark or flame. Due to the operating environment of underground mines, flash point is an important parameter. Provincial agencies in Canada and federal agencies in the US regulate the flash point of fuels allowable in underground mines. The flash point of biodiesel has been tested and reported by various sources. Specific testing at Southwest Research Institute concluded that the flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore pure biodiesel or blends of biodiesel with petroleum diesel is safer to store, handle, and use than conventional diesel fuel. In addition, the sulfur content of fuels utilized in underground mines is also regulated. Pure biodiesel is essentially sulfur free and results in a total reduction of $SO_2$ emissions as well sulfate aerosols in particulate matter. These reductions should assist in increasing both vehicle and catalyst life over time.

*Biodegradability*

Biodiesel also has desirable degradation attributes. Studies at the University of Idaho have been conducted to determine the biodegradation of biodiesel in an aqueous solution. Biodiesel was compared to diesel fuel and dextrose. Biodiesel samples degraded more rapidly than the dextrose control and were 95 percent degraded at the end of 28 days. The diesel fuel was approximately 40 percent degraded after 28 days.

Another study conducted at the University of Idaho tested the "Biodegradability of Biodiesel in the Aquatic Environment" by the $CO_2$ evolution method and gas chromatography (GC), comparing the results with regular diesel. According to the University of Idaho's report, under aerobic conditions and nutrient supply (N, P), microorganisms will metabolize a substance to two final products, $CO_2$ and water. Therefore, $CO_2$ is presumed to be the prevalent indicator of organic substance breakdown. If the substrate is the only carbon source, the amount of $CO_2$ evolved will be proportional to the carbons consumed by microorganisms from the test substrate. Thus, the percentage of $CO_2$ evolution is proportional to the percentage of substrate degradation.

The maximum percent $CO_2$ evolution from several samples of biodiesel produced were between 85.54-88.49 percent in 28 days, the same as that of dextrose, indicating there is no difference in their biodegradability. Yet, the $CO_2$ evolution from the diesel flasks was only 26.24 percent. It should also be noted that biodiesel blends accelerate the biodegradability of No. 2 diesel. For example a 20% biodiesel blend degrades twice as fast as No. 2 diesel. This illustrates that biodiesel use has demonstrated biodegradability benefits at levels lower than 100%.

*Toxicity*

Impacts on human health represent a significant criteria as to the suitability of a fuel for commercial applications. Health effects can be measured in terms of fuel toxicity to the human body as well as health impacts due to exhaust emissions. Tests conducted by Wil Research Laboratories, Inc. investigated the acute oral toxicity of pure biodiesel fuel as well as B20 in a single-dose study on rats. The $LD_{50}$ of pure biodiesel, as well as B20, was found to be greater than 5000 mg/kg, although hair loss was noted on one sample in the B20 group. The acute dermal toxicity of neat biodiesel was evaluated in a single dose study involving rabbits. The $LD_{50}$ of biodiesel was found to be greater than 2000 mg/kg and the 2000 mg/kg dose level was found to be a No Observable Effect Level (NOEL) for systemic toxicity.

Acute aquatic toxicity tests with Daphnia Magna have also been conducted. Table salt (NaCl), diesel, and biodiesel were compared to each other. The $LC_{50}$ count (the concentration where 50 percent of the Daphnia Magna have died and 50 percent were still alive) for table salt was 3.7 parts per million (ppm). Fifty percent of the Daphnia Magna were dead at 1.43 ppm for diesel fuel. The $LC_{50}$ number varied for biodiesel from 23 ppm to 332 ppm. Therefore, biodiesel is less toxic than diesel fuel.

## CONSIDERATIONS FOR BIODIESEL USE

*Infrastructure*

In general, the standard storage and handling procedures used for petroleum diesel should be used for biodiesel. The fuel should be stored in a clean, dry, dark environment. Temperature extremes should be avoided. Acceptable storage tank materials include mild steel, stainless steel, fluorinated polyethylene, and fluorinated polypropylene. Biodiesel has a solvent effect which releases the deposits accumulated on tank walls and pipes, which previously have been used for diesel. These deposits can be expected to clog filters initially and precautions should be taken to allow for this.

*Materials Compatibility*

Biodiesel over time will soften and degrade certain types of elastomers and natural rubber compounds. Precautions are needed when using high percent blends to ensure that the existing fueling system, primarily fuel hoses and fuel pump seals, does not contain elastomer compounds incompatible with biodiesel. Manufacturers recommend that natural or butyl rubbers not be allowed to come in contact with neat biodiesel. Biodiesel will lead to degradation of these materials. If a vehicle's fuel system does contain these materials, replacement with biodiesel compatible elastomers such as Viton B is recommended. The recent switch to low sulfur diesel fuel has caused most OEMs to switch to components suitable for use with biodiesel, but users should contact their OEM for specific information.

*Cold Flow Properties*

As with any diesel fuel, cold flow properties are important. A 20% blend of biodiesel will increase the cold flow properties (cold filter plugging point, cloud point, pour point) of petrodiesel approximately 1 to 3 degrees Celsius. Thus far, no precautions have been needed for fueling with 20% blends. Operation of neat (100%) biodiesel in cold weather, however, will experience gelling faster than petrodiesel. The solutions for this potential issue are much the same as that with low-sulfur #2 diesel (i.e., blending with No. 1 diesel, utilization of fuel heaters and storage of the vehicle in or near a building). Biodiesel appears to be unaffected by conventional pour point depressants.

*Fuel Availability*

The following companies have applied or are in the process of application to be listed as a biodiesel fuel supplier with the National Biodiesel Board. Any of these companies can be contacted for quotes on current price, supply, and distribution of biodiesel.

Ag Environmental Products (AEP)
9804 Pflumm
Lenexa, KS 66215

(800) 599-2121
Contact:  Bill Ayres or Doug Pickering

Twin Rivers Technology, Inc. (TRT)
780 Washington Street
Quincy, MA   02169
(617) 472-9200
Contact:  Biodiesel Sales

NOPEC Corporation
P.O. Drawer 2868
Lakeland, FL  33806-2868
(888) 296-6732
Contact:  Biodiesel Sales

Columbus Foods
800 North Albany
Chicago, IL   60622
(312) 265-6500
Contact:  Mike Gagliardo

Pacific Biodiesel, Inc.
285 Hukilike, B-103
Kahului, HI   96732
(808) 871-6624
Contact:  Bob King

*Economics*

There has been increasing interest in using diesel equipment in mines for reasons such as cost considerations.  Diesel-powered equipment is potentially less expensive to operate compared to other transportation systems and can increase productivity.  Safety is also an issue.  Some mine operators are interested in replacing electric trolleys used to transport miners with diesel-powered equipment because workers have expressed concern of electrocution by power lines and mine explosions caused by electrical sparks.  For these and other reasons, the number of diesel units being used in mines has been gradually increasing.

Concurrently, regulatory entities are considering the passage of stricter regulations for diesel powered equipment in underground mines.  These regulations are geared toward reducing the levels of exhaust emissions in mines.  Several industry sources do not believe that promulgating a strict particulate emission rule will have the desired effect of forcing development of low emission underground diesel engines as the potential market is too low.  These sources believe that the market for mine engines is too small to drive technology development itself.  The speed with which these technologies can be made available is dependent upon the length of the equipment development cycles.  Because many equipment types are highly specialized and relatively low volume, and because equipment manufacturers and their suppliers need to recover their investment costs before redesigning their products, development cycles are typically quite long.

Biodiesel offers the opportunity to utilize existing diesel engine technology and meet emissions reductions goals or enhance existing exhaust aftertreatment devices. Because biodiesel has a higher flash point than diesel and since it lowers emissions of particulate matter, carbon monoxide, oxides of sulfur, and potentially other air toxics, it could lower emissions levels in underground mines, reduce the cost of providing adequate ventilation in mines, and improve the performance of dry emissions systems by increasing the interval between servicing.

## SUMMARY

The use of biodiesel in underground mines is an easily implemented control strategy which has been demonstrated to reduce diesel particulate matter as well as other diesel emissions. The use of biodiesel substantially reduces the Ames mutagenicity of diesel particulates. Biodiesel compliments existing diesel and aftertreatment technologies (EGR, catalysts, filters, etc.) and can be used as a stand alone strategy or in combination with these future technologies. In addition, biodiesel is compatible with existing diesel fuel and provides the added benefit of improving lubricity and reducing sulfur and aromatics. Finally, biodiesel use provides other benefits to society such as reduction of $CO_2$, reducing dependence on foreign petroleum, and creation of domestic manufacturing jobs which make it an attractive option to help meet governmental and worker related goals.

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