



Lubrication®

A Technical Publication Devoted to the Selection and Use of Lubricants

Biodiesel and Engine Lubrication

Gary M. Parsons - Contributor

October 2007



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A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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ABSTRACT

There is a global interest in the use of alternative fuels due to the desire for energy independence, the high cost of petroleumderived fuels, and environmental concerns such as greenhouse gas emissions. Of particular interest is the use of biodiesel (esters of vegetable oil) which can be produced in all regions of the world, and is increasingly used in passenger cars as well as heavy-duty vehicles equipped with diesel engines.

Until now, much of the primary research has focused on process technologies to produce biodiesel from sources such as soy, palm, rapeseed, coconut and jatropha curcas. There have also been studies looking at the impact of biodiesel use on exhaust emissions, vehicle driveability, fuel economy, and fuel system compatibility. There is limited data on the impact of biodiesel use on engine lubrication.

In this two-part series of Lubrication Magazine, we will first discuss biodiesel composition, feedstocks and production techniques. We will also identify the primary benefits of biodiesel, as well as some of the concerns and challenges faced by the biodiesel industry. In addition, we will review the existing and emerging regulations that mandate the use of biodiesel in various regions of the world, as well as the Original Equipment Manufacturers' (OEM) positions regarding biodiesel use.

In the second issue, we will explore the impact of biodiesel use on engine lubrication through the use of bench tests, laboratory engine tests and real-world experience from fleets. Data will be included based on tests with biodiesel blends derived from soy, rapeseed, palm and coconut. We will also briefly discuss ways in which lubrication additive technology can help fortify the performance of the crankcase oil in order to counteract the effects of biodiesel use, such as increased oil oxidation and piston deposit formation.

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Part I

This is the first part of a two-issue series on biodiesel. Part I contains background information on biodiesel feedstocks, production and properties, plus Original Equipment Manufacturers' concerns regarding biodiesel use. Part II will provide laboratory and engine test data in which certain aspects of biodiesel use are evaluated with respect to engine lubrication.

Why All the Buzz About Biodiesel?

Today, countries worldwide are actively pursuing the development of programs to promote the production and use of biodiesel, a renewable fuel for diesel engines derived from a variety of plant oils and/or animal fats, or recycled cooking oils. Common plant-based feedstocks for biodiesel include soybeans, rapeseed, palm, corn, coconut and jatropha. Animal fats include pork lard, beef tallow, fish oil and poultry fat. The third source of feedstocks includes "float grease" from wastewater treatment plants and trap grease from restaurants, in addition to used cooking oils. By some definitions, biodiesel is considered to be biodegradable and suitable for sensitive environments. Biodiesel is a significant energy resource that may provide

part of the solution for complying with worldwide federal mandates to prevent and reduce pollution, diversify fuel sources and increase energy efficiency and sustainability.

What is Biodiesel?

According to the U.S. National Biodiesel Board (NBB), the terms "biodiesel" and "biodiesel blend" have specific technical definitions approved by ASTM International.

Biodiesel, n—a fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751.

Biodiesel Blend, *n*—a blend of biodiesel fuel meeting ASTM D 6751 with petroleumbased diesel fuel, designated BXX, where XX represents the volume percentage of biodiesel fuel in the blend.

Biodiesel blends may contain biodiesel in varying concentrations from one volume percent (B1) to 100 volume percent (B100). Diesel engines are capable of running on B100, although the practice is strongly discouraged by engine manufacturers, for reasons that will be explained later in this article. Typically dependent on blend credits



Emerging Biodiesel Market: Solving the Puzzle to Allow a Smooth Introduction



Well-to-Wheels Analysis-Petroleum System. Hydrocarbons Extracted from the Earth are Burned, Creating CO, Emissions

and taxation, the most popular biodiesel blends currently used in the U.S. are B2, B5, B11 and B20.

In addition to "biodiesel," there is "renewable diesel," which perhaps holds greater promise in the long term. The above represents the ASTM definition for biodiesel produced through a transesterification process to create a Fatty Acid Methyl Ester (FAME). However, it is important to understand that biomass can be handled and treated differently in other processes to create products that are not fatty acid methyl esters (FAME and mono alkyl methyl esters are identical). These other processes do not produce mono alkyl methyl esters, and are described later in this paper. They create products that are essentially straight chain saturated C15 and C17 alkyl chains, and are referred to as "renewable diesel." There are on-going debates regarding whether or not renewable diesel should also enjoy the incentives and subsidies designated specifically for mono alkyl ester biodiesel. The following discussion will, however, focus on biodiesel in the fatty acid methyl ester form.

So why is biodiesel of such global interest and importance?

Political and Economic Benefits – Biodiesel promotes a nation's energy security by making the nation more self-reliant and helps expand indigenous supplies of fossil fuels. Whether factual or not, there is also the common belief that use of renewable fuels can improve

a country's trade balance and enables funds spent on imported petroleum to be reserved within the national economy. According to the International Energy Agency (IEA), the U.S. consumes approximately 20 million barrels of oil a day (or 840,000,000 gallons), more than half of which is imported. By 2025, demand is expected to rise to 26 million barrels a day, of which 60 percent will be imported, states the U.S. Energy Information Administration (EIA). Annual expenditure on imported oil is now approximately 250 billion dollars. Moreover, this figure is increasing with the steady rise of oil prices to the \$90/barrel range. In addition to trade issues, fossil fuel alone cannot meet the projected global demand for liquid transportation fuels, meaning there is a shortfall. To make up for this shortfall, all forms of alternative sources are needed, including biofuels.

An additional motivation for the focus on biodiesel is the need to conserve the world's existing conventional fuel supply, which is currently being depleted at escalating levels each year. Fossil fuels such as diesel are nonrenewable, meaning that once their existing supplies are exhausted, they are gone forever. Biodiesel, on the other hand, is created from renewable resources that continue to be cultivated season after season, such as oils generated by plants from sunlight and air and fats produced by animals when



Well-to-Wheels Analysis - Biodiesel System CO, is consumed during Photosynthesis, Offsetting Some CO, Emissions

they consume food. Renewable fuels are considered more sustainable, as long as they are manufactured in an ecologically and environmentally acceptable way.

Emissions and Environmental Benefits - Biodiesel reduces global warming gas emissions such as carbon dioxide (CO_2) due to its closed carbon cycle. When biodiesel is harvested, processed and burned, some of the CO₂ released into the atmosphere is recycled by growing plants. These plants are later themselves processed into biodiesel, and the cycle continues. With fossil fuels, on the other hand, 100 percent of CO₂ generated escapes into the atmosphere. According to a 1998 biodiesel lifecycle study sponsored by the U.S. Department of Energy (DOE) and the U.S. Department of Agriculture (USDA), biodiesel reduces net CO₂ emissions by 78 percent compared to petroleum diesel. The reason it does not reduce CO₂ emissions by 100 percent is that fossil fuels are utilized in biodiesel production. Based on these results, the NBB has deemed biodiesel an effective greenhouse gas mitigation strategy for medium and heavy-duty vehicles.

According to the NBB, compared to emissions from diesel fuel, biodiesel also helps reduce ozone forming hydrocarbon (HC), poisonous carbon monoxide (CO) and hazardous diesel particulate matter (PM). Plus, biodiesel virtually eliminates acid rain-causing sulfur dioxide emissions. However, some studies have shown that the use of biodiesel does increase the oxides of nitrogen (NOx) emissions in most cases.

Agricultural Benefits – Biodiesel's primary feedstocks are soybean oil in the U.S. and Brazil, rapeseed oil in Europe and palm oil in Asia. With this important new end-use for these and other crops (such as jatropha, corn, cottonseed, etc.), there is enormous potential to stimulate global agricultural economies. Conversely, there are growing concerns regarding competing applications of edible feedstocks for food versus renewable fuels. These concerns will be addressed further in this paper, in the section on feedstocks.

Health Benefits – Scientific research has shown that compared to petroleum diesel exhaust, biodiesel emissions have lower levels of harmful polycyclic aromatic hydrocarbons (PAH) and nitrated PAH compounds. These compounds have been identified as potential carcinogens that can adversely affect reproductive, developmental, immunological and endocrine systems in both humans and wildlife. According to the DOE, using B100 can help to lower these toxins by up to 90 percent, whereas using B20 can eliminate 20-40 percent of them.

Furthermore, in 2000, biodiesel became the only alternative fuel to have successfully completed the Tier I and Tier II health effects testing of the 1990 Clean Air Act Amendments. Test results demonstrated that biodiesel has a non-toxic effect on health.

Fuel System Lubricity Benefits - As an ester, Biodiesel possesses favorable lubricity properties, which is important since all diesel fuel injection equipment relies somewhat on fuel as a lubricant, especially rotary and distributor type fuel injection pumps. Low lubricity fuel causes increased wear and consequently reduced component life. Biodiesel also contains less than 15 parts per million (ppm) of sulfur. The introduction of ultra-low sulfur diesel fuel (ULSD) renders biodiesel's lubricity of even greater significance, since ULSD as produced in the refinery can sometimes have poor lubricating properties, although this is easily rectified in terminals by the addition of lubricity additive. According to the NBB, bench scale testing has shown that even lowlevel biodiesel blends such as B1 and B2 can improve lubricity up to 65 percent without the need for additional lubricity additives.

Ease of Use and Safety Benefits – Biodiesel blends of B20 or less are literally a "drop in" technology, according to the DOE. However, not all Original Equipment Manufacturers (OEMs) agree with this assessment, as will be noted later. Biodiesel blends can be used in most diesel equipment with few, if any, modifications, and can also be used in the existing diesel fuel storage and distribution infrastructure. Plus, biodiesel is safer to use than petroleum diesel; the flashpoint for pure biodiesel (B100) is at least 260°F (130°C), versus a minimum of 125°F (52°C) for standard diesel. On the other hand, it must be noted that biodiesel (B100) is more aggressive towards certain elastomers and seals. Therefore, older fuel systems and distribution systems need to be inspected and modified before biodiesel can truly be considered a "drop in" technology.

Biodiesel Production Process

The two ASTM technical definitions limit the use of the term "biodiesel" to fuel that is produced when a plant oil or animal fat is subjected to a transesterification process, resulting in Fatty Acid Methyl Ester (FAME) with combustion properties very similar to those of petroleum-based diesel fuel. This FAME constitutes biodiesel. A byproduct of this process is glycerin, which is removed. Transesterification requires mixing the oil or fat with an alcohol in the presence of a catalyst. Alcohol choices include methyl, ethyl, propyl or butyl alcohols. Since methyl alcohol (methanol) is the most cost-efficient, it is the most popular choice. It also enables easier separation of the finished product from reaction byproducts. Depending on the alcohol used, the resulting biodiesel will be a methyl ester, ethyl ester, propyl or butyl ester respectively. Common catalysts include sodium hydroxide and potassium hydroxide. In the U.S., the main form of biodiesel is methyl soyate or soydiesel, formed by reacting methanol with soybean oil. The transesterification process reacts 100 units (by weight) of feedstock with 20 units of short-chain alcohol such as methanol in the presence of a catalyst, yielding approximately 100 units of biodiesel, 10 units of methanol (recovered from reaction) and 10 units of crude glycerin.



Typical Biodiesel Transesterification Process

Biodiesel Standards

In 2001, the ASTM approved the standard for biodiesel, designated ASTM D 6751. This standard pertains to pure biodiesel, known as B100, for use with petroleum diesel blends up to 20 percent by volume. Currently, work is underway to incorporate B5 into D 975, the petroleum diesel specification, as well as to develop separate specifications for biodiesel blends between B6 and B20. Not wanting to wait for an official ASTM B20 specification, on May 31, 2006, the Engine Manufacturer's Association issued a "Test Specification for Biodiesel Fuel" and has encouraged producers and users to follow it until an official ASTM specification is issued. The federal government has made ASTM D 6751 part of the official definition of biodiesel in the Energy Policy Act of 2005. Additionally, biodiesel, as defined in D 6751, is registered with the EPA as a fuel and a fuel additive under Section 211(b) of the Clean Air Act.

The European standards organization, Comité Européen de Normalisation (CEN) has also developed a performance standard for biodiesel fuel, EN 14214, which is considered to be stricter than ASTM D 6751. Its criteria are most easily met by methyl esters manufactured from rapeseed, which is the most common biodiesel feedstock in Europe. Although EN 14214 and ASTM D 6751 establish different values for properties such as viscosity and flash point, the most important distinction between the two is the measurement of oxidation and polymerization. Unsaturated oils oxidize faster and polymerize more rapidly than saturated oils. The Iodine Value (IV) measures the level of unsaturation in biodiesel. Consequently, a higher IV indicates a higher level of unsaturates, which in turn indicates an increased tendency to oxidize and polymerize. While EN 14214 establishes a maximum IV of 120 as well as an additional oxidation parameter called an Oxidative Stability Index, ASTM D 6751 does not incorporate an IV. However, it has recently been revised to include a threehour oxidation stability requirement. EN 14214 incorporates a more severe six-hour requirement. Since the soy methyl ester produced in the U.S. has a higher IV than the rape methyl ester in Europe, 130 versus 100 approximately, pure soybean oil methyl ester does not meet the requirements of EN 14214. With the looming shortage in Europe of rapeseed for biodiesel, EN 14214 may be relaxed to allow for the import of a wider range of biodiesel feedstocks, such as soy methyl ester. Currently, however, palm oil is being imported from Asia to make up for the shortfall in rapeseed.

Across the globe, many countries have either simply adopted the U.S. or European specifications, or adjusted them to fit their



Biodiesel is a Global Phenomenon

needs. For instance, although Canada supports ASTM D 6751, it has established a specification for biodiesel blends B1 through B5 called CAN/ CGSB-3.520 "Automotive Low Sulphur Diesel Fuel Containing Low Levels of Biodiesel Esters (B1-B5)." Australia, Indonesia and Brazil's biodiesel standards are a combination of ASTM D 6751 and EN 14214. Japan's biodiesel standard, JASO M360, is based on EN 14214, but with a more severe oxidation requirement. Thailand's biodiesel standard is also similar to EN 14214. In addition, Taiwan and Hong Kong are discussing standards similar to EN 14214. The Philippines' standard is specifically for B100 for CME (coconut methyl esters).

Biodiesel Feedstocks

A burning question today is how to supply the feedstocks necessary to produce the biodiesel mandated and/or subsidized by governments internationally. One concern is whether there is adequate arable land and water available to meet the growing demand. Additionally, there is a growing debate as to whether renewable fuels are being promoted at the expense of food.

In most regions, the primary feedstock for biodiesel is also used for human consumption, such as soybean oil in the U.S. and Brazil, rapeseed and sunflower oil in Europe, palm oil in Asia and canola oil in Canada. One result of the food vs. fuel debate is that the increased demand for edible feedstocks tends to inflate their price compared to non-edible feedstocks. Feedstocks account for 80 percent of biodiesel production costs and are the main reason that biodiesel is more expensive than conventional diesel fuel. According to the USDA, it takes about 7.3 pounds of soybean oil, which costs about 30-35 cents per pound, to produce a gallon of biodiesel. Feedstock alone, therefore, accounts for approximately \$2.45 per gallon of soy biodiesel. While fats and greases cost less and produce less expensive biodiesel, their supply is more limited and localized.

Some of the common international biodiesel feedstocks are:

Vegetable Oils:

Soybeans: The U.S. is the world's largest producer of soybeans, producing almost 38 percent of the world's crop in 2006. According to the USDA, in 2006 the U.S. produced approximately



84 million metric tons (mt) of soybeans. Brazil was a close second with 57 million mt. These figures are projected to increase yearly as additional acreage is devoted to soy production to meet the rapidly rising demand for biodiesel. However, a potential issue here is that both the U.S. and Brazil also have competing needs for ethanol, which requires the cultivation of arable land for corn and sugarcane instead of soybeans.

Rapeseed/Canola:

Rapeseed and canola is essentially the same crop, but canola is a version of rapeseed developed to lower the eruic acid to make the product safer for human consumption.



According to the USDA, in 2006, the EU produced 15.41 mt of rapeseed, while the U.S and Canada produced approximately 0.7 and 9.66 million mt of canola respectively. A large part of Canada's canola crop is exported to the U.S., and Europe is another potential export market due to its current rapeseed shortage. However, a problem for Canadian canola is the EU ban forbidding the import of genetically modified crops. This is currently under review by the EU due to its urgent need.

Palm Oil: According to the March 2006 Foreign Agricultural Service (FAS) crop assessment, Indonesia and Malaysia together accounted for over 85 percent of global supply, each country producing



approximately 15 million mt. Much of this is exported, especially to the EU. An issue of serious environmental concern is the practice of clearing tropical rain forests in order to make room for more palm oil plantations. Both countries have denied this practice and have announced measures to protect the rain forests. However, recently, the European Parliament has called for a ban on the use of biodiesel processed from palm oil, stating that the growing production of palm oil, sugarcane and soy in southeast Asia and South America is destroying tropical forests and other ecosystems, resulting in huge carbon dioxide emissions. They claim that carbon dioxide released from clearing and draining peat wetlands, and also forest fires in southeast Asia are related to the growing number of plantations for biodiesel production.

<u>Coconut:</u> The Philippines is the first nation to domestically produce and use coconut-derived biodiesel. In May 2007, the Philippine government introduced a biofuels act mandating all oil firms to blend one



per cent (B1) coconut-methyl ester in their diesel products. The Philippines' Department of Agriculture and the Philippine Coconut Authority (PCA) plan to develop 740,000 acres of land to meet the demand for expanded usage of coconut-methyl ester in diesel.

Jatropha Curcas (Physic Nut): Jatropha's major advantage is that it can be grown in virtually any tropical terrain and does not compete with food crops for arable land, thereby avoiding any issues with the food vs. fuel debate. However, unlike the byproducts of edible crops, the spent oil cake from jatropha cannot be fed to animals or used in applications where its toxicity is an issue. Jatropha is most popular in India, which has identified almost 100 million acres of land that could potentially be dedicated to jatropha without impacting edible crops or rain forests. If successfully cultivated, this acreage would produce approximately seven million gallons of biodiesel per year. Jatropha is also being planted in a number of African countries and in Guatemala and the Philippines. However, it should be noted that past attempts by the United Nations to establish Jatropha plantations and associated industries have not proved economic or successful.

Animal Fats/Tallow:

Only the lower grades of inedible tallow are candidates for the biodiesel pool since higher grades are absorbed by the chemical sector. Consequently, tallow is not a significant resource for U.S. biodiesel production. The lower grades have higher free fatty acid levels (FFA) and contain impurities, making pre-processing a necessary step prior to transesterification. A major issue with tallow-based biodiesel is its very high content of saturated fats, which translates to a methyl ester with poor cold weather qualities. The cold flow pour point of tallow-based methyl esters can be as high as 59° F (15° C), which is unacceptable even in warmer climates. Tallow of sheep and cattle is the primary biodiesel feedstock in Australia and is being considered for use in New Zealand.

Yellow and Brown Greases:



Biodiesel Feedstock Composition Impacts Performance

Other biodiesel feedstocks include the animal fats and vegetable oils used for cooking. Used cooking oil is sometimes called "yellow" grease, and although there is no strict definition, trap grease and sewage greases are referred to as "brown grease." The definitions of yellow and brown grease are blurred and are often based on the degree of oxidation, color and FAA content. Due to resource limitations, recycled cooking oil alone is not a viable solution for the energy crisis. However, it is sometimes the feedstock of choice for small biodiesel plants. The biggest drawback of these greases is their variable nature- they often contain deposits that must be filtered out, and have high FFA levels. They must undergo a series of pre-treatment processes in order to meet the minimum quality requirements for transesterification.

Feedstocks Influence Biodiesel Properties

Biodiesel's properties depend heavily on the specific feedstock used, which is a challenge for the industry since it is critical to ensure consistent quality among the various blendstocks. Each animal fat or vegetable oil molecule used to produce biodiesel via transesterification is composed of a glycerine backbone of three carbons, to each of which is attached a long chain fatty acid. These long chain fatty acids react with methanol to make the methyl ester or biodiesel, and may be saturated, monounsaturated or polyunsaturated, depending on the feedstock

used. The differing levels of saturation determine the properties of finished biodiesel. Biodiesel made from feedstocks that contain highly saturated fatty acids, (such as palm and coconut oils, beef tallow and yellow grease), has a high cetane number and superior oxidative stability. It also helps reduce NOx emissions. One downside is that this biodiesel has poor cold weather properties; it exhibits high cloud and pour points, which means it tends to start forming crystals much too soon for use in colder climates. On the other hand, biodiesel made from oils with high polyunsaturated content, (such as soy, canola and sunflower oils), has lower cloud and pour points, which make for better cold weather properties. However, it has a lower cetane number and poor oxidative stability, and also tends to produce higher NOx emissions. It is possible to impact the varying properties of different biodiesel fuels by the use of additives.

Challenges of Biodiesel

High Cost – Biodiesel generally costs more to manufacture than petroleum diesel, resulting in a wholesale price that is typically higher by \$1-\$2 per gallon, according to the DOE. Traditionally, B20 has been priced about 20 cents more than diesel fuel while B2 has been only a few cents more. The price difference is primarily due to high feedstock costs, and renders biodiesel uncompetitive with petroleum diesel. Currently the biodiesel



Not all Engines Appreciate Biodiesel: Catastrophic Failure Caused by Biodiesel Use without Adjusting Maintenance Intervals and Using Compatible Lubricants

industry is reliant on a plethora of federal and state programs, subsidies, production incentives and tax credits. For instance, federal blend tax credits of \$1 and \$0.50 per gallon exist in the U.S. for biodiesel produced from agricultural and non-agricultural feedstocks respectively. Similar tax credit schemes are used in other countries. Critics argue that in order for biodiesel to be enduringly successful as a viable industry, it must be economically self-supporting.

Lower Energy Content - According to the DOE, biodiesel (B100) contains approximately 8.5 percent less energy per gallon than typical No.2 petroleum diesel fuel. This is due to the oxygen content in the ester molecules of biodiesel, which essentially means that the molecule is already partially reacted (combustion is the reaction between carbon and hydrogen with oxygen). Therefore, one can think of biodiesel as partially burnt by about 12 percent. The difference in density between FAME and mineral diesel then results in the per gallon difference in energy content of approximately 8.5 percent as stated above. One gallon of No. 2 diesel contains 129,050 BTUs, while one gallon of biodiesel contains 118,170 BTUs. While this difference in energy content is often imperceptible with respect to power, torque and fuel economy in engines using blends up to B20, it can definitely be noticeable with B100. Since fuel accounts for up to 50 percent of a truck fleet's cost, small differences in cost and energy content (fuel economy) can result in a significant impact on truck fleet profitability.

Poor Cold Weather Performance – Biodiesel freezes or gels up in cold weather sooner than petroleum diesel, due to its relatively high pour point temperature. As the fuel gels, it becomes increasingly viscous, clogging fuel filters and hindering the passage of fuel from the tank to the engine. Cold weather properties are the major reason that many people use biodiesel blends as opposed to neat biodiesel, B100. The NBB recommends that the same cold weather performance solutions, (kerosene and cold flow additives), that are utilized with No.2 diesel fuel, should also be used with B20. While B20 usually raises fuel cold weather properties such as cloud point, pour point and filter plugging point by 2-10°F, B5 and B2 have virtually no impact on cold flow. Biodiesel's cold flow properties are heavily dependant on feedstock selection, as described earlier in this article.

High Solvency Effect - Biodiesel has a tendency to dissolve accumulated sediments in diesel storage and engine fuel tanks, due to the superior solvency properties of methyl esters. These dissolved sediments can then plug fuel filters. Sometimes the filters burst, propelling sediment through the fuel injector system to cause injector deposits and potential failure. The solvency effect is much greater with high blends of biodiesel compared to B20 and lower blends. Therefore, before B100 is used for the first time in tanks or lines previously used for petroleum diesel, it is important to clean the tanks and fuel systems thoroughly to remove old sludge and deposits. It is also advisable to check fuel filters frequently and change them as necessary.

Materials Compatibility – Pure biodiesel degrades, softens or seeps through some hoses, gaskets, elastomers, seals, glues and plastics with prolonged exposure, which can create fuel system leaks. Nitrile rubber compounds, polypropylene, polyvinyl and Tygon materials are especially susceptible. Using biodiesel blends higher than B20 can damage fuel systems components such as hoses and pump seals, which contain elastomers incompatible with biodiesel. In this situation, users should consider replacement with compatible elastomers. However, this is primarily an issue with older engines manufactured before 1993, according to the DOE. The recent switch to ULSD has meant most OEMs have converted to components that are also suitable for use with biodiesel. B5 and lower blends have not exhibited elastomer deterioration and may not require modifications.

B20 and higher biodiesel blends will degrade and create sediments after prolonged contact with bronze, brass, tin, copper, zinc and lead. Copper pipes and fittings, brass regulators, zinc linings and lead solders should also be avoided. Biodiesel is hydroscopic, meaning it attracts moisture. Once it comes in contact with moisture, it can hydrolyze and form a variety of organic acids which are partly responsible for its compatibility problems with various seal, elastomers, and metals.

Low Oxidative Stability – Biodiesel has lower oxidative (long-term storage) stability than petroleum diesel. Factors affecting biodiesel's oxidative stability include the degree of saturation of the feedstock, the level of natural antioxidant content, carbon chain length and the presence of glycerides. In biodiesel, fuel aging and oxidation can create high viscosity, high acid numbers and the formation of filterclogging varnish and sediments. The NBB recommends a six-month maximum storage life for B100. If the fuel is kept longer, antioxidants should be added and periodic tests should be performed to ensure the fuel continues to meet the ASTMD 6751 specification. Suitable storage tank materials are steel, aluminum, fluorinated polyethylene, fluorinated propylene and Teflon. Some suppliers use nitrogen blanketed storage vessels to reduce the tendency of stored biodiesel to oxidize and to help keep moisture and condensation out of the tank.

Increased NOx Emissions - Biodiesel causes a slight increase in emissions of ozoneforming nitrogen oxides (NOx), according to the DOE. The precise composition of biodiesel influences NOx emissions. There is around 15 percent NOx variability among the various biodiesels meeting ASTM D 6751, with soybean oil-derived biodiesel creating the highest increase in NOx due possibly to reactions with its high polyunsaturated fatty acid content. Although biodiesel itself contains very little bound nitrogen, NOx is created in the engine as nitrogen and oxygen in the intake air react at the high in-cylinder combustion temperatures. Some effort is being made to solve this problem with the use of exhaust after-treatment systems in newer engines, but the possible increase in the NOx levels when biodiesel is used in older engines is a concern. There are research efforts underway by the California Air Resources Board (CARB) and by the EPA to define the problem of NOx increase more precisely. Some past work has indicated the increased NOx is related to differences in injection rates into the combustion chamber caused by biodiesel's higher viscosity and bulk modulus, which makes it less compressible than petroleum diesel. The higher bulk modulus and higher speed of sound of biodiesel means the pressure rises in the fuel lines and develops an advance of nearly two degrees in injection timing. This in turn generates a faster pressure and temperature rise in the combustion cylinder, leading to an increase in NOx.

Second Generation Biodiesel and Biomassto-Liquid (BTL) or "Renewable Diesel"

Today's FAMEs are considered first generation biodiesel. In spite of enormous investment efforts, this biodiesel alone is not sufficient to fulfill growing global energy demand and there are concerns regarding

product quality. Therefore, the spotlight is shifting to what is called second generation and third generation, or renewable diesel, which has the potential to cover a greater portion of world energy demand. Unlike biodiesel, second generation renewable diesel is manufactured in oil refineries using a chemical process similar to the conversion of crude oil into motor fuel. Third generation renewable diesel can be obtained from lignocellulosic sources such as straw, timber, woodchips, plant waste or manure. Since the technology allows renewable diesel to be produced from any plant material, this would eliminate the competition between food and fuel as well as the finished product quality concerns that are intrinsic to first generation biodiesel production. The main source of raw materials for energy would shift from arable land to forests, peat bogs, and crop and municipal residue. The process is called biomass-to-liquid (BTL), in which the previously pelletized biomass is directly gasified at low pressure. The resulting synthetic gas is purified and then converted into a liquid diesel fuel using a catalytic conversion process like the Fischer Tropsch synthesis reaction. Unlike first generation biodiesel, the properties of the finished second or third generation renewable diesel product are independent of the feedstock.

While first and second generation biodiesel is mainly produced from grain kernels only, third generation biodiesel is manufactured from the entire plant, offering the prospect of much higher yields. Plus, a significant environmental advantage of third generation biodiesel is its lower greenhouse gas emissions. It has a smaller carbon footprint since the amount of energy-intensive fertilizers and fungicides remains unchanged for a far greater output of useable material.

There are two sizeable obstacles that need to be overcome before third generation biodiesel arrives at the pumps—technology and cost. The BTL production process is much more complicated than transesterification. Relatively high manufacturing expenditure means that third-generation biodiesel cannot yet be produced economically on a large scale. However, ultimately it offers higher potential for production and cost reductions, because it can be sourced from biowaste with fewer competing end-uses. Consequently more research projects are being launched worldwide for the purpose of developing biomass-based processes to commercial maturity. Two second-generation renewable diesel projects are highlighted below:

Neste Oil's NExBTL® Technology

Finland's Neste Oil has developed NExBTL®, which stands for NExt generation Biomass To Liquids diesel technology, and incorporates a unique approach of combining natural renewable raw materials with traditional oil refining processes. It is similar to "H-Bio," the second generation biodiesel developed by Italy's ENI and Brazil's Petrobras. The process consists of hydrogenating fatty acids across a nickel-molybdenum catalyst under high pressure. It can use multiple plant oil feedstocks and animal fats to create a superior product with characteristics similar to ultraclean synthetic biodiesel. The advantage of NExBTL® and the similar H-Bio technology is that it can be fully integrated in existing oil refineries, and the finished fuel properties are largely independent of the feedstock. Such refineries already have hydrogenation facilities, therefore renewable diesel units can be more easily incorporated into existing plants. The first NExBTL® plant started production this year in Porvoo, Finland, with a capacity of 170,000 tons a year.

NExBTL® is sulfur-, oxygen-, nitrogen-, and aromatic-free and has a very high cetane number. It can have acceptable cold weather properties, good storage stability, low water solubility and also reduces exhaust emissions. However, the distillation curve is different from that of mineral diesel and the lack of light ends has some Original Equipment Manufacturers (OEMs) concerned about cold start problems if B100 were to be used in cold climates. NExBTL® biodiesel is compatible with the existing diesel fleet as well as with diesel logistics systems, and is technically easy to blend in conventional diesels in all ratios. The EU has approved NExBTL® as a certified EU diesel fuel.

Neste has labeled NExBTL® as "renewable" diesel to distinguish it from traditional biodiesel, a distinction that may prohibit the fuel from enjoying some incentives and mandates designated specifically for mono alkyl ester biodiesel. This issue is currently being discussed in the U.S., where the \$1 per gallon tax credit for biodiesel would apply for NExBTL® today, based on an Internal Revenue Service ruling that was issued in April 2007. The NBB, amongst others, is challenging the ruling.

ConocoPhillips and Tyson Foods Unite to Produce Second Generation Biodiesel

In April 2007, meat producer Tyson Foods and oil company ConocoPhillips announced plans to work together to produce second generation renewable diesel fuel from pork and poultry fat. Using a proprietary thermal depolymerization production technology, the animal fats will be processed and then fed along with hydrocarbon feedstocks to a hydrotreater unit, to produce a high-quality diesel fuel that meets all federal standards for ultra-low-sulfur diesel. The final product has a high cetane value, and the processing step improves storage stability and handling characteristics compared to biodiesel created by transesterification. The benefit of treating the animal fats this way is that the finished product could be passed through multiproduct pipelines just as ultra-low-sulfur diesel is today.

The two companies estimate that the operation could result in 175 million gallons of renewable diesel a year. As previously mentioned, animal fats and cooking greases alone cannot solve the energy crisis. To put things in perspective, the U.S. consumed approximately 62 billion gallons of diesel in 2006, according to the DOE. Thus, ConocoPhillips and Tyson's contribution would constitute less than one percent of the overall diesel consumption.

The companies are expecting to be able to take advantage of the \$1 per gallon tax credit that will make the fuel cost effective. Although the tax credit is set to expire in 2008, it is likely to be extended given the government's commitment to ensuring that biodiesel stays competitive with regular fossil fuel diesel.

National Biodiesel Accreditation Program: BQ-9000

Biodiesel fuel quality is of paramount concern and importance to the biodiesel industry. For this reason, the NBB has established a quality assurance program called BQ-9000 for the accreditation of biodiesel producers and marketers. The primary objective of BQ-9000 is to ensure that biodiesel is consistently manufactured per the ASTM D 6751 standard. BQ-9000 combines the ASTM standards with an integrated quality program that includes storage, sampling, testing, blending, shipping, distribution and fuel management practices. To receive accreditation, companies must pass a rigorous review and inspection of their quality control processes by an independent auditor. There are two types of accreditation; Accredited Producer and Certified Marketer.

A national fuel quality testing project, cofunded by NBB and the NREL, discovered that 59 percent of biodiesel samples taken between November 2005 and July 2006 were out of specification for incomplete processing, containing trace quantities of un-reacted di- and tri- glycerides. These unreacted components will also combine with natural sterols in biodiesel, leading to large molecules that will not pass through filters. This is the same issue that caused some filter clogging problems in Minnesota in winter, since cold weather can amplify problems caused by out-of-specification fuel. The NBB/NREL test results indicate that some producers are not correctly monitoring the quality of their biodiesel, and help to underline the importance of BQ-9000.

Germany and Austria have established a similar program called the "Arbeitsgemeinschaft Qualitätsmanagement Biodiesel" (AGQM) or the "Labor Group for Biodiesel Quality Management." This organization includes many service stations that offer biodiesel, which have pledged to sell only rape methyl ester (RME) since it is the sole form of biodiesel approved by certain original equipment manufacturers (OEM).

Original Equipment Manufacturers (OEMs) and Biodiesel

All engine and vehicle OEMs provide a material and workmanship warranty on their products. These warranties do not cover problems caused by external factors out of their control, such as fuel variations. Therefore, the most important points regarding engine warranties and biodiesel are whether an OEM will void its warranty when biodiesel is used, and whether the fuel supplier will stand behind its fuels in case of trouble. Existing and potential users of biodiesel should consult with their OEM representatives to determine what the terms and conditions of their warranty coverage might be. Local laws and regulations vary in this respect.

Position of U.S. OEMs

All major OEMs have stated formally that the use of biodiesel blends up to B5 (and in some cases B20 and even

B100) will not void their parts and workmanship warranties, provided the biodiesel meets ASTM D 6751. Some OEMs also recommend that biodiesel be purchased solely from BQ-9000 certified companies. Certain OEMs even fuel their new diesel vehicles with biodiesel blends in the factory, such as John Deere with B2 and Case IH with B5. Chrysler also fills all its diesel-powered Jeep® Libertys, Dodge Rams and Jeep Grand Cherokees with B5. Furthermore, the Energy Policy Act (EPAct) encourages municipalities and non-combat military vehicles to use B20 by allowing fleets to meet part of their alternative fueled vehicle (AFV) acquisition target through purchase credits awarded for the use of B20 or higher blends. This has compelled some OEMs to warrant B20 use in these applications. For instance, Chrysler has approved B20 use in its Dodge Ram pickup trucks for government, military and some commercial fleet customers.

The NBB, together with major OEMs, has formed the B20 Fleet Evaluation Team (B20 FET) to develop a position on the use of biodiesel blends up to B20 in diesel engine applications in the U.S. The B20 FET has identified a list of recommendations for users dated June 2005 and titled, "Technical Recommendations for B20 Fleet Use Based on Existing Data." This also applies to blends over B5 and below B20, such as B11, which is popular in Illinois. While this list is not intended to replace warranty limitations established by individual OEMs, it is a statement of confidence that B20 can be used trouble free if appropriate precautions are taken. Simultaneously, the NBB is also actively working with the ASTM to develop a separate standard for B20. This will be critical in enabling OEMs to increase their recommended biodiesel blend level to B20. As previously mentioned in the section on standards, the EMA has issued a B20 "Test Specification for Biodiesel Fuel," and work is also ongoing to create distinct specifications for blends up to B5, and between B6 and B20.

Position of International OEMs

In Europe, since the EN 590 standard permits diesel fuel to contain up to B5 without being labeled, in practice, the user has no idea which blend is actually filled at the pump. As a result, most major heavy-duty and passenger car European OEMs have been compelled to accept B5. They will honor their warranties with the use of biodiesel blends up to B5, provided the biodiesel meets EN 14214. Currently, the EU is investigating the possibility of allowing up to B10 in the EN 590 standard in 2008.

The Japanese heavy-duty OEMs allow the use of up to B5 in their engines, provided the neat biodiesel meets JASO M360, the Japanese specification introduced in April 2007. It is similar to EN 14214, but incorporates more severe oxidation requirements.

Below is a table that lists some of the OEMs' current positions on warranties with the use of biodiesel blends. Since these often change, the end user is strongly advised to consult the specific OEM before utilizing any level of biodiesel blend.

OEM Concerns with Biodiesel

OEMs are worried about biodiesel's impact on three key engine components - fuel system, lubricant performance and emissions system.

While B5 is generally considered safe, users of higher concentrations of biodiesel have reported fuel system problems such as corrosion and deposits in injection systems and compatibility issues with rubber seals in fuel systems. While biodiesel's effect on engine lubrication is not completely understood, one definite fact is that its higher density, surface tension, and viscosity relative to mineral diesel creates fuel dilution in the crankcase and engine corrosion issues plus sludge and piston deposits. Most OEMs will honor their warranties in the case of these higher blends more or less on a case-by-case basis, and only if their recommendations are implemented. However, major diesel injection manufacturers Denso, Delphi, Siemens VDO

| Manufacturer | Warranty Position |
|--|--|
| Case IH | All engines approved for up to B5 and most for up to B20. Must meet ASTM D 6751 or EN 14214 |
| Caterpillar | Many engines approved for B30 and B100, others limited to B5. Must meet ASTM D 6751 or EN 14214 |
| Cummins | Most post-2002 engines approved for up to B20, must meet ASTM D 6751 |
| Daimler/Chrysler | All engines approved for up to B5 and some for up to B20. Must meet ASTM D 6751 |
| Detroit Diesel | Approve up to B5, must meet ASTM D 6751 |
| Ford | Up to B5, must meet ASTM D 6751 or EN 14214 |
| General Motors | All engines approved for up to B5 and some up to B20. Must meet ASTM D 6751 |
| International | Approve up to B20, must meet ASTM D 6751 |
| John Deere | All engines approved for up to B5, must meet ASTM D 6751 or EN 14214 |
| Mack | Up to B5, must meet ASTM D 6751 |
| Mercedes-Benz | Up to B5, must meet ASTM D 6751 plus have the necessary oxidation stability (min. 6h, proved with EN14112 method) to prevent damage from deposits and/or corrosion |
| New Holland | Up to B20, must meet ASTM D 6751 |
| Scania | Up to B5 and also B100 with reduced drain intervals. Must meet EN 14214 |
| UD Trucks/Nissan Diesel | Up to B5, must meet EN 14214 or ASTM D 6751 |
| Volkswagon | Up to B5, must meet EN 14214 or ASTM D 6751 |
| Volvo | Up to B5, must meet EN 14214 or ASTM D 6751 |
| Fuel Injection Equipment Manufacturer | |
| Bosch | Up to B5, must meet EN 14214 |
| Delphi | Up to B5, must meet ASTM D 6751 |
| Siemens VDO | Up to B5, must meet EN 14214 or ASTM D 6751 |
| Stanadyne | Up to B20, must meet ASTM D 6751 |
| Denso | Up to B5, must meet EN14214, ASTM D 6751, or JASO M360 depending on region |

and Bosch will not honor their warranties with the use of biodiesel blends above B5. Stanadyne, on the other hand, will warrant up to B20.

The increasingly strict emissions regulations oblige the OEMs to use extremely precise equipment, as well as guarantee in-use emissions compliance for an extended duration (for example, 10 years or 485,000 miles for heavy-duty trucks in the U.S.) Biodiesel poses an unknown factor in this equation – it has not been the subject of any certification work, and its impact on emissions and emissions system durability is not yet fully known. Moreover, various biodiesel blends may potentially impact emissions in different ways. Many believe the OEMs should not be responsible for differences in emissions levels due to biodiesel use.

While the use of B5 is generally trouble-free in the case of older diesel passenger cars and heavy-duty trucks without diesel particulate filters (DPFs), increasing problems have been detected in newer engines with DPFs. In some applications, OEMs are using a late "post" injection to help regenerate DPFs. This late injection may create higher levels of fuel dilution. Biodiesel is more persistent once it enters the crankcase and thermally decomposes forming insolubles and deposits. OEMs have noted situations where fuel dilution rates ran up to 15 percent in vehicles operated with DPF and post injection.

In order to address some of these issues, most European OEMs prescribe a 50-70 percent reduction in oil drain intervals with the use of biodiesel blends above B5. For instance, in the case of Mercedes Benz trucks, this means service intervals decrease from 100,000 km to 30,000 km, a 70 percent reduction. Unfortunately, for large fleets, these reduced service intervals are fiscally unattractive, and act as a deterrent to the use of biodiesel blends above B5. This, along with biodiesel becoming more expensive as subsidies expire, has led to a drop in usage of biodiesel in some countries. For instance, the German government is reducing some of its many subsidies and tax incentives for biodiesel, effectively eliminating the financial advantage.

Pure Plant Oils

Some German fleet operators have replaced B100 with pure plant oils, which do not meet EN 14214. These oils have created numerous issues for OEMs and operators, including cold-start difficulties, corrosion and elastomer degradation. A similar situation also arose in Brazil, where some fleets were motivated by price to mix vegetable oil directly with diesel, resulting in engine failures. It is for this reason that biodiesel is strictly defined as a mono alkyl methyl ester (same as a fatty acid methyl ester). Pure plant oils generally have high viscosities and contain substances that will form gums and deposits in fuel systems, and as such are not acceptable for use in modern diesel engines.

- Fuel System
 - Injector deposits
 - Fuel filter plugging
 - Injection pump durability
 - Materials incompatibility
 - Fuel Instability
 - Low temperature handling
 - May reduce detergency and anti-foam properties of fuel additive packages



Emissions Systems

- Impact on aftertreatment devices and sensors
- Impact on NOx emissions
- Lower BTU content/fuel economy
- Lubricant Performance
 - Fuel dilution
 - Corrosion
 - Viscosity increase
 - Oxidation
 - Piston Deposits
 - Sludge Deposits
 - Wear







Crankcase Fuel Dilution with Biodiesel-Properties of Biodiesel Lead to Higher Fuel Dilution Levels than Mineral Diesel

Part I-Summary

In this first part of a two-issue series, the reader has gained a basic understanding of the nature of biodiesel, current and future biodiesel production techniques, and some of the concerns and issues being faced by the industry. In Part II, we will focus on diesel engine oil lubrication performance when biodiesel is used. Bench tests as well as laboratory engine test data will be presented.



Crankcase Fuel Dilution with Biodiesel-Higher and Narrower Biodiesel Boiling Range Makes it More Persistent Once Inside the Crankcase

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