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Understanding Biodiesel Fuel Quality and Performance

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The purpose of this paper is to provide the reader with sufficient information to understand Biodiesel fuel quality and the effect various quality parameters have on diesel equipment performance. The American Society of Testing Material (ASTM) test methods are used as a basis for drawing comparisons between regular diesel fuel and Biodiesel. Failure to control the processes for manufacturing, blending and storage of Biodiesel can lead to performance problems in all types of diesel fueled equipment.

Biodiesel is produced from vegetable oils, recycled cooking greases and animal fat. A basic overview for manufacturing Biodiesel is provided below (See Figure 1).

Biodiesel Manufacturing Process

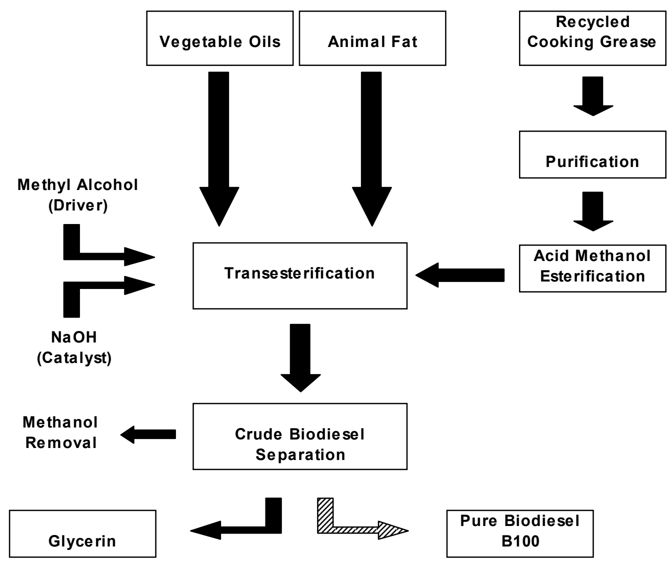

Figure 1

Biodiesel is manufactured in both the United States and Europe. There are currently seven (7) manufacturers in the United States[1]. Manufacturing diesel fuel from vegetable oil, recycled cooking grease or animal fat reduces the dependency on petroleum based oil, however, because of the number of variations in feedstock oils, their chemistry and the controls used in the manufacturing process, it costs more to produce Biodiesel then regular diesel fuel.

The chemistry involved in manufacturing Biodiesel is uncomplicated and entails a single step transesterification reaction. Chemicals such as methyl alcohol and sodium hydroxide are used to convert the oil or fat feedstock to fatty acid methyl esters (FAME's). The major by-product glycerin is more polar and higher in density than the FAME's. This causes the glycerin to readily separate during the reaction. Glycerin can be easily removed from the Biodiesel or FAME's once the reaction is complete. Because the process is relatively simple, numerous entrepreneurs make various Biodiesel type fuels in their back yard and there are manufacturers of salad oils who have found it convenient to produce Biodiesel as an added capability to their processes.

Requirements for the quality of manufactured Biodiesel are established by ASTM D6751, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels[2]. Currently there are no ASTM methods in place for the feedstock oils or fats that are used, nor are there standards for consistent quality control of the transesterification process. There is a debate within the Biodiesel industry over how much control and whether current test method limits for the end product Biodiesel quality are rigid enough. Tighter controls could improve the Biodiesel quality but would be more costly for the manufacturers, feedstock suppliers and ultimately the consumers. The fact that poorly produced Biodiesel will operate diesel equipment even with large variations in quality is at the heart of the industry controversy.

Biodiesel users need to understand that variations in Biodiesel quality can go unnoticed for months before affecting engine/equipment operation or creating problems in storage. The fuel quality deterioration once started is irreversible.

Pure Biodiesel, referred to as B100, is typically produced to be mixed with Number 1(kerosene) and/or Number 2-diesel fuel. Blends of 80 % diesel fuel and 20% B100 are referred to as B20. **Table 1** below shows a comparison of property temperature ratings for No. 1 and No. 2 diesel fuels, B100 and a diesel fuel blend. Because of the inherent higher temperature Cloud Point, Pour Point and Cold Filter Plug Point of B100, it is necessary to mix B100 with blends of Number 1and Number 2-diesel fuel in the North where colder temperatures exist. This will keep the fuel from solidifying in tanks and fuel systems. Typically in the South, B100 can be mixed with Number 2 diesel without concern with storage and operating temperatures. B100 and Biodiesel blended diesel fuel solidify when the individual, mixed or combined temperatures are lower than the values shown in **Table 1**. Operating diesel equipment on Biodiesel below these temperature ratings will result in plugged fuel systems and the inability to start or run equipment. Currently there are no ASTM test limits for Cloud Point for either B100 or regular diesel fuel, nor are there any test requirements for Pour Point or Cold Filter Plug Point.

Table 1

	#1 Diesel	**#2 Diesel**	**B100**	**50/50 #1/#2 Diesel Blend**
Cloud Point	-54 F	4 F	32 F	-6 F
Pour Point	-70 F	-30 F	25 F	-45 F
Cold Filter Plug Point	-30 F	1 F	22 F	-12 F

The differences between Biodiesel and petroleum based diesel fuel are important to understand. **Table 2** below shows a comparison of the ASTM test requirements for B100 (D6751) and regular diesel fuel (D975) [2]. An asterisk (*) denotes variances in the defined Test Method Limits, variances in Test Methods, or where Test Method Limits are not established or required.

Table 2

		ASTM D6751 (B100)	**ASTM D975 (Diesel)**
Property	**Test Method**	**Limits**	**Limits**
Flash Point	D 93	130 C	* #1 38 C #2 52 C
Water & Sediment	D 2709	0.05 max %volume	0.05 max %volume
Kinematic Viscosity, 40C	D 445	1.9-6.0 mm^2/s	* 1.3-4.1 mm^2/s
Sulfated Ash	D 874	0.02 max %mass	*
Ash	D 482	*	0.01 max %mass
Sulfur	D 5453	0.05 max %mass	*
Sulfur	D 2622/129	*	0.05 max %mass
Copper Strip Corrosion	D 130	No. 3 max	No. 3 max
Cetane Number	D 613	47min	* 40 min
Aromaticity	D 1319	*	35 max %vol
Cloud Point	D 2500	Report C	*
Cloud Point (Operability)	D 4539/6371	*	C max (undefined)
Carbon Residue	D 4530	0.05 max %mass	*
Acid Number	D 664	0.8 max mg KOH/g	*
Free Glycerin	D 6584	0.020 max %mass	*
Total Glycerin	D 6584	0.240 max %mass	*
Phosphorus Content	D 4951	0.001 max %mass	*
Distillation Temp (90% Vol Rec)	D 1160	360 max C	*
Distillation Temp (90% Vol Rec)	D 86	*	282 C min – 338 C max
Ramsbottom Carbon	D524	*	0.35 max %mass

The significance of these variances can be understood by looking at the differences in characteristics of fuel made with vegetable oil, grease or fat, and petroleum based fuels. The Specific Gravity of a FAME fuel is typically 0.88 and is not the same as regular diesel fuels. Diesel fuels can vary between SG=0.85 for No. 1 diesel and SG=0.92 for No. 2 diesel. This, along with polarity differences, will cause a B20 blend of regular diesel fuel and Biodiesel to separate over time and should be kept in mind when storing B20 for extended periods. Pure Biodiesel is about 11 % oxygen by weight due to the number of methyl ester fatty (carboxylic) acids. Since methyl esters contain oxygen, with the formula $-CO_2CH_3$, the FAME fuel contains oxygen. Diesel fuel on the other hand is derived from crude oil and is purely hydrocarbon, composed of about 15 % aromatic and 85% aliphatic hydrocarbons containing no oxygen. The primary significance of this will be in the heating value of the fuel. The heating value for B100 is approximately 16,000 BTU's/LB and for Number 2 diesel fuel is approximately 18,000 BTU's/LB. The presence of oxygen in B100 makes Biodiesel less carbon-rich than regular diesel fuel, however, an advantage of having an oxygenated fuel is that the oxygen is readily available for combustion and the combustion process takes place more completely than with non-oxygenated fuels.

Flash Point, Viscosity, and Distillation Temperature can be correlated directly to the quality of a FAME fuel (B100). The values for each of these can vary as B100 or a B20 blend ages, residual methanol carries over in the B100, or if the diesel fuel being mixed with B100 is light (No. 1 diesel) or heavy (No. 2 diesel). When monitoring the quality of Biodiesel, the fuel viscosity measurements tend to follow Distillation Temperature measurements. The maximum acceptable test limit for Distillation Temperature at 90 % is 640 degrees F for diesel fuel and 680 degrees F for B100. If for example a Distillation Test at 90 % for blended B20 indicates that 640 degrees F limit is exceeded, it is up to the user or operator to determine if the fuel is acceptable for use. Normally this would not be a problem unless both the viscosity and Distillation Temperatures were out of limits according to ASTM D975. B20 fuel that tests above limits in viscosity and Distillation Temperatures should not be used because of the greater risk of plugging fuel lines and equipment shutting down.

If on the other hand the diesel fuel being mixed with B100 is a blend of light fuel oils, the resulting B20 mixture can have a lower Flash Point. Residual methanol in B100 carried over from the manufacturing process can also cause a lower than normal Flash Point in a B20 blend. Although it would be difficult for a diesel equipment operator to determine whether lower Flash Point or higher Distillation Temperatures are related to the B100 or the diesel fuel used in the blend, actions should be taken to determine the cause of distinct variations in quality readings. Low Flash Point values coupled with high Distillation Temperatures in diesel fuel will cause engines to start poorly, particularly in the winter. If a low Flash Point is caused by methanol carryover in the B100, a B20 Biodiesel blend will deteriorate rubber components in a fuel system. Because there is not an ASTM specification for a B20 blended diesel fuel, it is recommended that ASTM D975 limits for Flash Point, Viscosity and Distillation Temperature be adhered to for establishing the quality of a B20.

Table 3 below shows a comparison of ASTM D6751 Acid Number limits for B100 and acid test results of B100 from three (3) different suppliers. Acid Number is a good indicator of the level of Free Fatty Acids in Biodiesel. High tested values for Acid Number can be correlated to manufacturing a FAME fuel from unrefined feedstock (i.e. high in Free Fatty Acids) and/or poor process control in the conversion of the feedstock oils or fats to a FAME fuel (i.e. methanol carryover). Note in **Table 2** above there is no defined limit for Acid Number for diesel fuel and the test limit for B100 is considered by the authors to be high when comparing actual test results from the suppliers in **Table 3**. High acid levels in Biodiesel can cause fuel system deposits and is another indicator that the fuel will act as a solvent resulting in the deterioration of rubber components of a fuel system.

Table 3

		Limit (D6751)	**Supplier #1**	**Supplier #2**	**Supplier #3**	**Supplier #4**
Acid Number	D 664	**0.8 max mg KOH/g**	0.18	0.32	0.17	Not Meas'd

Clearly there is a difference in the solvency tendency when comparing the above supplier B100 to the limits for Acid Number in ASTM D6751 (0.8 max mg KOH/g). Because there is not an Acid Number test limit for a B20 blend, a diesel fuel equipment operator would not know how to gage the solvency tendency of the B20 biodiesel fuel being used, or whether the pure Biodiesel (B100) in the blend was manufactured with good process controls. Furthermore, should moisture be present in transport or storage tanks, the methyl esters in the Biodiesel will degrade quicker resulting in further increases in Acid Number. Moisture causes the methyl esters in Biodiesel to undergo hydrolysis forming Free Fatty Acids. At this time neither the ASTM D6751 nor D975 test methods contain a test requirement for evaluating the level moisture in petroleum products (ASTM D6304). Water in a B20 blend is also soluble with any remaining methanol and glycerin carried over from the manufacturing process. Over time this can cause stratification of the fuel. Diesel fuel and the FAME's of unhydrolyzed B100 will tend to remain in the other layer of stratified fuel. Moisture is very common in diesel storage tanks and should be minimized or eliminated when storing Biodiesel. Users of Biodiesel should monitor the Acid Number when the fuel is received and during storage to see if the Biodiesel is susceptible to degradation or if degradation is occurring. Normally moisture would not present a problem with diesel fuel or diesel equipment, however, moisture is detrimental when combined with any Biodiesel product and would ultimately affect both equipment performance and equipment maintenance. Another concern with moisture presence in diesel fuel storage is the possibility of the formation of bacteria. If algae appear in Biodiesel storage tanks it can be treated with a Biocide. It is recommended that periodic testing be done to ensure microorganisms are not present in diesel fuel storage tanks. The authors have found that when moisture is present in Biodiesel degradation fuel by hydrolysis to Free Fatty Acids is more of a problem to the user than bacteria growth.

The type of oil or fat used in the Biodiesel manufacturing process will influence many of the properties in **Table 2** above. Most of the pure Biodiesel (B100) fuel manufactured in the United States has been produced using Soybean oil feedstock. There are many other vegetable oils available (i.e. Coconut, Peanut, Cottonseed, Corn, etc.) as well as recycled cooking oil (i.e. waste or used restaurant greases), and animal fat (i.e. chicken, beef, pork) that can be used to manufacture Biodiesel. Each of the vegetable oils, recycled cooking greases, and animal fats will vary in the make up and content of saturates, polyunsaturates and fatty acids. Furthermore, the oils, greases and fats can be either refined or unrefined prior being entered into the Biodiesel manufacturing process. Oils that are more saturated such as Coconut or Palm Kernel will produce a more stable Biodiesel. Biodiesel produced from oils such as Soybean and Linseed that are more unsaturated will be less stable. All variations in feedstock affect the transesterification process controls, the amount of chemicals used in the reaction, and the end product characteristics of the FAME fuel. Research done by the National Renewable Energy Laboratory in Golden, Colorado found that when comparing different feedstock oils to manufacture Biodiesel, "high levels of saturates (C14:0, C16:0, C18:0) raise cloud point, raise Cetane number, reduce NOx, and improve stability, while more polyunsaturates (C18:2, C18:3) reduce cloud point, reduce Cetane number, raise NOx, and reduce stability"[3]. Polyunsaturates in the feedstock oils have a known propensity to auto-oxidize with air to form cross-linked, insoluble matter. Their reactivity increases with an increase in sites of unsaturation, and in particular, the number of methylene groups between two double bonds. For example, Soybean oil is high in linoleic fatty acids (50 to 60 %) and linolenic fatty acids (2 to 10 %) and is therefore susceptible to auto-oxidation in the presence of air. Limiting air exposure during storage or using feedstock that contains fewer sites of unsaturation will negate this undesired side reaction. The degree of unsaturation in feedstock oils, greases or fats therefore determines how much chemicals and reaction time is needed in the manufacturing process to produce stable Biodiesel. A stable Biodiesel fuel, including blends, will have an acceptable shelf life and test well within required ASTM limits. An unstable Biodiesel fuel will test in the upper limits or out of limits for many of the ASTM test methods described above, and will be predisposed to the formation of less combustible components. These less combustible components are characterized as a cross-linked or oxidized insoluble matter (i.e. appears as varnish).

The test method for Total Glycerin correlates directly to the stability of pure Biodiesel (B100). In **Table 4** below is a comparison of the Free and Total Glycerin properties for four different suppliers of B100. Note that the Total Glycerin in the B100 from Supplier #4 is slightly over the ASTM D6751 test limit while the other three suppliers are significantly under the same test limit.

Table 4

		Limit (D6751)	**Supplier #1**	**Supplier #2**	**Supplier #3**	**Supplier #4**
Free Glycerin	D 6584	**0.020 max %mass**	0.002	0.010	0.003	0.004
Total Glycerin	D 6584	**0.240 max %mass**	0.128	0.015	0.092	0.265

Even though the B100 from Supplier #4 is only slightly over the test limit for Total Glycerin, the value indicates elevated levels of glycerin. High glycerin content in the fuel indicates poor manufacturing. Users of B100 from Supplier #4 would begin seeing clogged fuel filters and residue formation in their fuel systems and storage tank components in less than six (6) months of operation. On the other hand, users of B100 from Suppliers 1 through 3 would find that their Biodiesel would not rapidly degrade or cause them equipment performance related problems even if the Biodiesel was stored for an extended period of time. The effects of fuel degradation or aging will depend on the operating parameters of the diesel equipment. High temperature engines, which are normally run at high speeds for long periods of time, can use fuels that have a higher viscosity. Under these performance conditions, the use of aged or degraded fuel may not affect engine operation. In the case where engines are run intermittently or at cooler temperatures, it would not be good to use an aged Biodiesel with elevated viscosity, Flash Point, and/or Distillation Temperature. Engines operating under these performance conditions would show decreased power, increased smoke and odor, and deposits would form in the engine and fuel system.

The best way to ensure Biodiesel provides trouble free operation is to monitor several quality parameters of both the B100 and Biodiesel blends used in operation. Any B100 or Biodiesel blends that do not meet established quality parameters should not be accepted or used. In addition, there are other steps that can be taken to help ensure trouble free equipment performance and extend the life of your Biodiesel. These include:

1. Rank suppliers of B100 by quality and pricing. It may be better for your operation to spend a more for better quality Biodiesel, particularly if your operation is in colder climates, the Biodiesel sits in fuel tanks or is stored for extended periods of time, and is intermittently used in equipment operations.
2. Require a Certificate of Analysis of the B100 from the manufacturer according to the ASTM D6751 Test Method. Reject any B100 that fails to meet any of the D6751 test limits. Consider establishing an ongoing sampling and testing program that monitors the quality of the Biodiesel and Biodiesel blends over time.
3. Take steps to ensure transport and storage containers of both B100 and Biodiesel blends are free of moisture and other contaminants such as dirt. Perform periodic inspections to be sure shipping containers, transport tanks, and storage containers do not show signs of moisture or contamination.
4. For large storage volumes (i.e. greater than 500 gallons) of Biodiesel blends (i.e. B20), install a re-circulation and filtration (10 micron) system. This provides the user the means to mix different blends of pure B100 and diesel fuels, as well as, reduces the dependency on an intermediate fuel supplier.
5. Perform quarterly or semi-annual filter changes on any Biodiesel equipment with fuel filters.
6. Turnover Biodiesel fuel inventories in equipment and storage tanks every 6 to 12 months. Do not operate vehicles with Biodiesel if the vehicle can not burn one full tank of fuel within 2 months.
7. Establish these limits for acceptability of B100 in addition and as an alternative to those found in ASTM D6751.

Total Glycerin	D6584	0.15 max % mass
Cloud Point	D2500	-5 C max
Flash Point	D93	100C
Acid Number	D664	0.4 max mg KOH/g
Ramsbottom Carbon	D524	0.090 max %mass
Particulate Contamination	D6217	40 mg/L max
Water in Petroleum Products	D6304	500 ppm max
Micro-Organism Culture		Negative
Micro-Organism Bacteria		None

In conclusion, operating diesel equipment on Biodiesel is good for the environment and US economy. Biodiesel characteristically reduces engine friction and heat, and is biodegradable. Engines fueled with Biodiesel blends will emit lower CO, CO2, particulate, soot and hydrocarbons. It is hopeful the technical information and discussions provided in this paper will help with the success for those who are currently using Biodiesel or are considering using Biodiesel as an alternative fuel. If you are interested in additional information or have questions on the content of this paper, please contact Mike Weiksner at mike.weiksner@srs.gov.

References:

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