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Feasibility Study for the Use of Biodiesel in the Caltrans Fleet

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Feasibility Study for the Use of Biodiesel in the Caltrans Fleet

Final Report

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Abstract

Over the past several years, biodiesel use has dramatically increased due to its potential emissions benefits, classification as a low-carbon/renewable fuel and ability to be integrated into diesel fleet applications without significant infrastructure or other substitution issues. Caltrans has largest fleet in California, so biodiesel would provide many benefits in terms of meeting environmental and energy security objectives. However, all aspects of biodiesel use needed to be thoroughly investigated, including potential benefits and liabilities, prior to widespread introduction into the Caltrans fleet. In this research project, the University of California, Riverside (UCR) completed a thorough literature investigation, surveyed current users, attended national technical sessions designing the strategic road-map and reviewing the progress for biodiesel, wrote specifications for Caltrans purchase of biodiesel and carried out a twelve-month field demonstration at Indio. Results of the research and field demonstration showed that biodiesel is a viable option for Caltrans. A caveat moving forward is that each site should carry out a thorough analysis of the implementation to include the cleanliness of their fuel tanks and the assurance that the delivered fuel meets ASTM D6751 specifications and the specified low temperature flow properties.

The research recommended that emissions be measured with Caltrans equipment rather than relying on published values and that work is being carried out in a follow-on Caltrans project.

Keywords: biodiesel, fleet management

Executive Summary

Caltrans has the largest and most diverse mobile fleet in California and strives to meet progressive goals in reducing emissions, displacing petroleum, utilizing emerging technologies, and staying ahead of government regulations. Biodiesel is a fuel that offers a number of potential advantages to the Caltrans fleet including opportunities of cleaner air, compliance with the low carbon/renewable fuels standards and easy substitution. However, before incorporating a new fuel in its fleet, Caltrans must carefully review many factors. The factors include the issues associated with operability/warranty of the fleet vehicles, increased cost due to the fuel switching and the impact on the environment. Results of the field test revealed reliability was maintained and the fuel was widely accepted by the operators. Cost was higher but manageable within the time frame of the testing. Cost increases should decline as the renewable fuel standard is implemented in California.

Caltrans had not tested biodiesel due to the potential of increased NO_x emissions. In the context of issues related to the environment, there is a reduction in toxic emission levels but there is an increase in NOx. A complete evaluation of biodiesel was proposed by the University of California, Riverside (UCR) in order to insure a smooth introduction of biodiesel within the State and to identify areas/applications that would benefit most from biodiesel use.

Given this background, UCR's research project specifically addressed: 1) biodiesel compatibility with Caltrans' diverse fleet of engines and exhaust retrofits, 2) emissions benefits and/or debits, 3) commercial availability and pricing of biodiesel for purchase, 4) specifications for biodiesel purchased by Caltrans, 5) regional issues e.g., air quality, weather, etc., impacting the use of biodiesel by Caltrans, 6) optimum biodiesel blend ratio, 7) miscibility with other diesel fuels, 8) emissions and petroleum reduction calculations, and 9) regulations, including those of the California Air Resources Board, as well as other legal considerations that may have bearing on the use of biodiesel in California. The deliverables include: 1) a thorough literature search and survey of the issues stated above and 2) demonstration of biodiesel blends in selected Caltrans vehicles/equipment and locations.

Findings from this project include:

- Biodiesel is the most advanced alternative diesel fuel currently available. A literature review shows that most state Department of Transportation (DOT) organizations have been satisfied with their use of biodiesel blends, B5 and B20. Some data are available on pure biodiesel use.
- Biodiesel meeting the highest quality standard, BQ 9000, is both produced and distributed in California. Production of biodiesel is growing rapidly and a recent national tax incentive of $1 per gallon for virgin feeds and 50¢ per gallon for used feeds has helped provide a product that is more cost competitive with diesel.
- A biodiesel blend with diesel fuel (B20) was successfully used in existing equipment at a Caltrans facility in Indio for one year without disruptions in meeting the operating schedule. The fuel was utilized in a variety of conditions, from desert heat to colder mountain weather operation. Equipment operators and drivers all indicated that the B20 performed as well as typical diesel fuel.

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- While biodiesel is relatively easy to implement into existing fleet operations with the existing diesel fuel infrastructure, it has solvent-like properties that may release deposits in storage or on-vehicle fuel tanks. These released deposits may plug fuel filters. For B20, the incidences of these problems are expected to be minor. Our recommendation is to utilize some additional precaution in fuel filter maintenance and related issues, but not to implement special practices that would be expensive on a fleet-wide basis.
- Biodiesel has ASTM fuel specification, ASTM 6751, and quality control/assurance program, BQ9000, for producers and distributors. In June of 2008, the ASTM committee adopted a modified petrodiesel specification ASTM D975 to include blends of up to 5 volume percent of biodiesel and created a new stand alone specification to handle bends of biodiesel up to 20 volume percent.
- Fuel quality surveys over the last several years have shown that biodiesel fuel quality can vary significantly, although it is improving. The BQ9000 standard initiated by the biodiesel industry is an important step to standardizing the quality of the biodiesel produced around the country. It is strongly recommended that Caltrans utilized to extent possible producers or distributors that are BQ9000 certified.
- Biodiesel use can cause operability problems in low temperature environments without the proper purchase specifications. During the summer 2008, UCR provided Caltrans with recommended specifications for all Caltrans Districts in California.
- Biodiesel does impact exhaust emissions. Most studies show a switch to B20 reduces CO, HC and PM, but increases NO_x slightly, by about 2-3%. Research published in 2008 provided insight as to the source of the NO_x increase, the impact of engine load and operation on the NO_x increase, and ways to mitigate the increase. The NO_x increase will disappear with the installation of NO_x exhaust control technologies that will be implemented on new engines in upcoming years.
- Caltrans should monitor CARB's ongoing comprehensive study of biodiesel emission benefits and debits that is being carried out by these authors at UCR. This study will provide the basis for fuel formulations that will be developed for the mitigation of the biodiesel NO_x increase that will be implemented throughout the State. It is also suggested that Caltrans also conduct some direct studies of the emissions impact of biodiesel in Caltrans equipment and applications, since the emissions impacts are a function of engine load and operation. This work is currently being carried out in a follow on Caltrans study.

1 Introduction

1.1 Caltrans Push for Alternative Fuels

Caltrans has the largest and most diverse mobile fleet in California and strives to meet progressive goals in reducing emissions, displacing petroleum, utilizing emerging technologies, and staying ahead of government regulations. In 2006, a policy letter calls for Caltrans to "demonstrate proactive stewardship on shifting the State dependence on standard fuel sources." (see Appendix A) Biodiesel is an alternative fuel that offers a number of advantages to the Caltrans fleet including opportunities of cleaner air, compliance with fleet/fuel rules and easy substitution. However, before incorporating any new fuel in its fleet, Caltrans must carefully review many factors. These factors include the issues associated with operability/warranty of the fleet, costs due to the fuel, and the impact on the environment. Caltrans had not yet tested biodiesel due to the potential of increased NO_x emissions, for example. In the context of these issues, a complete evaluation of biodiesel was proposed by the University of California, Riverside (UCR) in order to: 1) insure a smooth introduction of biodiesel, 2) identify areas/applications that would benefit most from biodiesel use, 3) understand the benefits/debits of biodiesel on emissions and performance, and 4) avoid potential risks to fleet equipment, public safety and air quality.

1.2 Why Biodiesel

By definition biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM (American Society for Testing & Materials) D 6751. The use of biodiesel offers many advantages, and among the most important of these advantages is that biodiesel is a renewable fuel and the energy used to produce the fuel is only a small fraction of the per gallon energy content of the product. Biodiesel has the best energy balance of any liquid fuel. Some alternative fuels are criticized for using as much energy to make the fuel as the fuel contains. This is not the case with biodiesel. Every unit of fossil fuel energy needed to produce biodiesel results in 3.2 units of fossil fuel energy (Sheehan et al., 1998). Thus use of biodiesel provides petroleum displacement and global warming gas emission reductions. Additionally, biodiesel also has a number of composition properties that leads to lower emissions of particulate matter and other criteria pollutants from diesel engines.

Biodiesel use is an inviting path for government and other fleets that require alternative fuels to earn credits toward compliance of the Energy Policy Act (EPAct) that Congress passed in 1992 to reduce the nation's dependence on imported petroleum. The Energy Conservation Reauthorization Act of 1998 (ECRA) amended EPAct to allow credit for biodiesel use. Compliance with EPAct is met by credits awarded for acquisition of alternative fuel vehicles (AFVs) or using an alternative fuel. For example, one biodiesel fuel use credit, which is counted as one AFV acquisition, is allocated to fleets for each purchase of 450 gallons of neat biodiesel fuel, for use in diesel vehicles more than 8,500 lbs. GVWR. The biodiesel must be neat (B100) or in blends that contain by volume at least 20% biodiesel and 80% petrodiesel (B20). Fleets are allowed to use these credits to fulfill up to 50% of their EPAct requirements. These credits can be claimed only in the year in which the fuel is purchased for use, and they cannot be traded among fleets. Authorization for biodiesel use by the US military in non-tactical vehicles was approved in 1999. This approval was initially limited to biodiesel derived from virgin soybean oil, but was recently extended to include biodiesel made from yellow-grease.

Like any emerging product, there are significant milestones that lend recognition to its acceptance in the market and help advance the growing use. For biodiesel the first milestone was when the American Society of Testing and Materials (ASTM) issued specification, D 6751-02, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels. ASTM is the premier standard-setting organization for fuels and additives and their action standardized fuel quality and increased the credibility of biodiesel in the eyes of consumers and engine manufacturers. The ASTM specification is for the final product and allows the manufacture from any vegetable oil or animal fat as the raw material. Recently, the ASTM issued specifications for neat biodiesel and for diesel blends containing up to 20 volume percent of biodiesel.

A second significant achievement was when biodiesel became the only alternative fuel in the United States to have successfully completed the EPA's Tier I and Tier II Health Effects testing under Section 211(b) of the Clean Air Act. Tier I testing demonstrated biodiesel's significant reductions in most currently regulated emissions as well as most unregulated emissions. Results of Tier II testing showed that biodiesel's emissions had a non-toxic effect on human health.

A third incentive was financial when the Congress recognized the need to support the fledgling biodiesel industry. Towards that end, the Congress implemented a tax credit of $1 per gallon for those using virgin feed stocks and half that amount for re-cycled feed stocks. This legislative action makes biodiesel more cost competitive with petroleum diesel fuel.

In summary, there are a number of reasons and advantages why biodiesel is gaining in market penetration, wide spread acceptance, and should be considered for use by Caltrans.

- Biodiesel and biodiesel blends with petroleum-based diesel fuel can be used with the current fueling infrastructure and in all diesel engines with little or no engine modification.
- Biodiesel is easy to phase in and out, allowing flexibility in technology deployment.
- Users receive one EPAct credit for every 450 gallons of biodiesel purchased. Users of B20, which is 20% biodiesel, receive one EPAct credit for every 2,250 gallons used.
- Biodiesel is reported to reduce emissions of some criteria pollutants and air toxics; however, it may increase NO_x emissions, which the most critical issue in using biodiesel in non-attainment areas

1.3 Project Tasks and Objectives

In the University of California, Riverside (UCR) response to the Request for Proposal from Caltrans, we offered the following Tasks and sub-tasks in order to assure Caltrans would have a smooth introduction of biodiesel in their fleet.

1.3.1 Task 1: Literature and Field Application Review and Survey

The literature and field application review was comprehensively reviewed including all aspects of biodiesel use, equipment compatibility/warranty, fuel (specification/availability/cost/petroleum displacement), emissions, and regulations.

Task 1.1 Fuel Specifications

UCR conducted a comprehensive evaluation of the specifications used for biodiesel and biodiesel blends. UCR reviewed specifications utilized by the military and general services administration for biodiesel use. UCR also reviewed the specifications and levels approved by the Engine Manufacturers for each engine type represented in the CalTrans fleet, including the blend levels approved for warranty compliance. UCR evaluated the potential of a B20 specification, which is currently not provided under ASTM specifications. A recommended specification(s) was provided for CalTrans based on this analysis.

Task 1.2 Fuel Storage and Handling

UCR evaluated issues related to the storage and handling of biodiesel. The literature will be reviewed on issues such as the oxidation stability of biodiesel, cold weather performance, and chemical additives to improve performance. Recommendations were provided on any special storage requirements for biodiesel or biodiesel blends. Recommendations were also be provided for use of biodiesel under cold weather conditions. The use of additives to improve characteristics of biodiesel blends was also included in any recommendations.

Task 1.3 Pricing and Availability

UCR surveyed all know suppliers of biodiesel to determine the price and availability of biodiesel throughout the state. The survey included information about the base feedstock material used for each of the marketed biodiesels. Estimates of the potential expansion of the biodiesel market will be obtained based on contacts with NREL, the NBB, and the open literature. Regulations pertaining to biodiesel tax credits and EPAct credits and their impact on costs will also be reviewed.

Task 1.4 Emissions Impacts

A comprehensive evaluation of the literature pertaining to the emissions benefits/liabilities of biodiesel was performed. This included general biodiesel emissions data compiled by industry, government and in peer reviewed literature. The literature review also emphasized studies more relevant to Caltrans, including those related to off-road equipment and engines and those utilizing fuels meeting California specifications. A model being developed under an ongoing Caltrans study was also be expanded to incorporate the emissions effects and petroleum displacement of biodiesel in the Caltrans fleet. Based on information gathered in this subtask, a determination was made as to whether additional in field emissions tests will be needed.

Task 1.5 Regulatory Elements

UCR evaluated regulations on a state and federal level pertaining to biodiesel and biodiesel use. This included regulations dealing with tax credits, as well as those dealing with biodiesel specifications, emissions requirements, or limitations on the sale of biodiesel.

1.3.2 Task 2: Field Demonstration Project

This task describes a field demonstration project that will be conducted in Caltrans equipment, mainly vehicles, with oversight and reporting conducted by UCR.

Task 2.1. Development of Demonstration Test Plan and Site Selection

A comprehensive test plan was developed prior to initiating the field demonstration program. The test plan included the number of sites and vehicles/equipment and duration of the field test. The test plan described the reporting elements of the demonstration include recording of fuel economy, maintenance records, emissions, if needed, and other requirements. Recommendations on the use of biodiesel including specifications, handling and storage requirements, and blending ratios were also included. A contingency plan was also included to return the vehicles/equipment to regular diesel in the case of problems that cannot be resolved. The test plan was developed in conjunction with Caltrans staff to insure adequate coverage and scope, and insure the availability of the sites and vehicles/equipment.

Task 2.2. Implementation and Evaluation of Biodiesel in the Field

Biodiesel was implemented into the field at each of the locations specified in the test plan. A preliminary kick-off meeting was held at each fleet location as needed. Throughout the course of the field demonstration, records was maintained of fuel consumption, mileage, maintenance, and any other issues related to the biodiesel use, handling, or storage. Periodic site visits and conference calls were conducted throughout the demonstration period, to ensure smooth implementation of the biodiesel and that adequate records are being maintained.

Task 2.3. Compilation and Evaluation of Demonstration Results

Records of fuel consumption/mileage, maintenance, and other items was collected throughout the course of and at the end of the field demonstration. Records for fuel consumption/mileage and other items were compared to similar measurements made on the control equipment during use on regular diesel to provide a comparison of differences in fuel consumption. Maintenance records were also surveyed to note/determine if the biodiesel fuel results in any abnormal maintenance issues or provides additional performance benefits. The fuel storage and handling procedures used in the demonstration program was assessed to determine if they are adequate for a more complete implementation of biodiesel into the Caltrans fleet and recommendations will be provided in fuel-related areas where improvement can potentially be made. Additionally, modeling runs were performed for each of the sites to determine the emissions and petroleum displacement benefits of biodiesel use over the demonstration period.

2 Literature Review of Biodiesel Manufacture

2.1 What is Biodiesel?

Biodiesel is often referred to as a clean burning alternative fuel, produced from domestic, renewable resources such as vegetable oils, (for example; soybean oil), recycled restaurant grease, and animal fats. The National Biodiesel Board suggests that organizations seeking to adopt a definition of biodiesel for purposes such as federal or state statute, state or national divisions of weights and measures, or for any other purpose, use the following definition to be consistent with other federal and state laws and Original Equipment Manufacturer (OEM) guidelines as follows:

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D 6751 specifications for use in diesel engines. Biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel blends are denoted as, "BXX" with "XX" representing the percentage of biodiesel contained in the blend (B20 is 20% biodiesel, 80% petroleum diesel).

Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D 6751) in order to insure proper performance. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments. Biodiesel that meets ASTM D6751 and is legally registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the EPA, and it is not a legal motor fuel.

2.2 Biodiesel Feedstocks

All feedstocks, presently used and those under research, breakdown along two major groups: vegetable oils and yellow grease/animal fats. All are organic in nature, agriculturally derived and produced annually: It is critical to pinpoint the information about feedstocks as feedstock supply and cost are the key economic factors in determining the outlook for biodiesel availability and affordability.

Vegetable Oils: Biodiesel can be produced from a number of different feedstocks including soy oil, rapeseed (canola) oil, palm oil, coconut oil, walnut and other sources. Soy-oil is the most commonly used feedstock for biodiesel in the United States. The soy bean industry has been a major driving force behind biodiesel expansion due to excess production capacity, product surpluses and declining prices. Soy-oil is the least expensive vegetable oil and represents over 75% of the total virgin vegetable oil market. The National Renewable Energy Laboratory (NREL) estimated that sufficient supply of excess soy-oil represented approximately 304 million gallons/year in the US in 2001 (Tyson et al., 2004). These crops are grown commercially as agricultural products. These crops are consistently produced annually and are therefore renewable in nature.

Yellow-Grease and Animal-Fats: Yellow-grease and animal-fats are also organic and derived from agricultural means. Both are sought after as they are normally much lower cost than soy oils, leading to a more profitable and affordable biodiesel product. The animal fats (tallow)-based biodiesel have some problems with use at low temperatures.

1. **Yellow-Grease**--Yellow-Grease or used cooking oil is another commonly used feedstock in the US. It is recycled restaurant cooking oil which has been rendered into a tradable commodity by removing water and solid matter. Restaurant cooking oil is often hydrogenated soybean oil. Therefore, this feedstock is derived from an agricultural crop which is organic and renewable in nature. Additionally, as America's demand for fast-food continues to increase, so will the production of cooking oil derived from soybean oil. The growing biodiesel market is providing an additional value-added market for yellow-grease. This market is important as it helps eliminate yellow-grease from the waste stream which reduces stress on waste water treatment facilities, as well as issues around it being put into landfills.

The average supply of yellow-grease in the US is sufficient to produce a maximum of 344 million gallons of biodiesel. There are some limitations on use of the available supply to produce biodiesel in that it is estimated that only 55% of the biodiesel industry is capable of process yellow-grease feedstocks (Alternative Fuels Data Center, 2005). The Energy Information Agency indicates biodiesel production would be limited to 100 million gallons per day due to competing uses for the product (Radich, 2006).

2. **Animal-Fats**--Feedstocks derived from animal-fats can also meet the definitional standard for qualification as biomass. Animal-Fats used for biodiesel production are derived from rendering animal carcasses from large production farms, dairies, feedlots, and meat-packing plants. The oil produced from the rendered carcasses is then used as a feedstock for producing biodiesel. Just as oilseed planted crops are renewable in that they are capable of being replaced by a natural ecological cycle, so too are livestock. However, a major difference arises in the intended purpose for raising the two products. These differences must be accounted for in describing how the various feedstocks meet the definitional standard for qualifying as biomass. While oilseeds are produced for their oil content, the oil produced from animal rendering is derived from the waste by-products of meat and dairy production.

Other feedstocks are more commonly used for biodiesel production in overseas countries. In Europe, the rapeseed oil is the most ready utilized feedstock for biodiesel production. In areas of Southeast Asia, palm oil is the most readily available feedstock for biodiesel production. Research on additional feedstocks also continues in the US. Researchers at the University of Idaho have investigated the potential for seed oils from the brassicaceae family, which includes canola, rapeseed, and mustard, as a potential biodiesel source crop in the Pacific Northwest (Van Gerpen, 2006). Their estimates indicate that use of canola, rapeseed, and mustard in the Pacific Northwest could supply up to 125 million gallons of new oil for biodiesel. NREL is also looking at algae sources for biodiesel, such as seaweed and kelp, as part of its Aquatic Species program.

Federal excise tax credit is a key consideration with respect to feedstock selection. With the federal excise tax credit, the cost for the feedstock is reduced and biodiesel is more affordable for the consumer. The credit equates to one penny per percent of biodiesel in a fuel blend made from virgin agricultural products like vegetable oils or other first-use materials such as animal fats that have not been used before, such as in frying. Recycled or second-use oils also receive a tax credit, but it is on one-half penny per percent of biodiesel used in a fuel blend. As such, there is a tradeoff between feedstock costs and the tax credit that must be considered in using different biodiesel feedstocks. The tax incentive is taken at the blender level, meaning petroleum distributors, and passed on there to the consumer. The tax credit is currently applicable through December 31, 2008.

2.3 Chemistry of Diesel and Biodiesel Feedstocks

The feedstock for petroleum based diesel fuel is crude oil and other streams boiling in the distillate range. A close inspection of the chemistry would reveal there are thousands of compounds that can be grouped into four broad classes: paraffins, naphthenes, olefins and aromatics. The first two groups are considered saturates hydrocarbons and the latter groups unsaturated hydrocarbons, Other classifications might group the polynuclear aromatics and hetero atoms where the nitrogen, sulfur and oxygen molecules are found. The boiling range of the diesel product is broad and encompasses molecules from nine to twenty –three carbon atoms and centered about sixteen carbon atoms as shown in Figure 2-1.

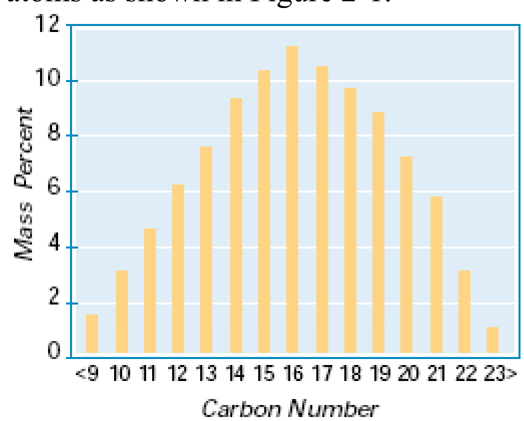

Figure 2-1 Typical Carbon Number Distribution for #2 Diesel

The chemistry and carbon number distribution differ dramatically for biodiesel and petroleum diesel feedstocks in that the range of the carbon atoms for biodiesel is rather narrow as shown in Table 2-1. For example, biodiesel feedstocks typically contains up to only 14 different types of fatty acids that become chemically transformed into fatty acid methyl esters (FAME) instead of thousands of compounds. While the number of carbons atoms is centered on C18, like #2 petrodiesel, the distribution on average is rather narrow. However, wider variations between the various biodiesel feedstocks are found, depending on the vegetable or fat oil. The chemical compound differences for each biodiesel feedstock have a profound influence on the properties of the finished biodiesel. For example, high levels of saturates (C14:0, C16:0, C18:0[1]) raise cloud point and cetane number; more unsaturates (C18:2, C18:3) reduce cloud point and cetane number. Appendix C shows the structural formula for some of the common fatty acids found in biodiesel.

[1] Nomenclature: C18:2 is a hydrocarbon molecule with 18 carbons and 2 olefinic bonds.

Fatty Acid Fat or Oil	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0 C22:0	C20:1 C22:1	Other
Tallow	--	--	0.2	2-3	25-30	2-3	21-26	39-42	2	--	0.4-1	0.3	0.5
Lard	--	--	--	1	25-30	2-5	12-16	41-51	4-22	--	-	2-3	0.2
Coconut	5-9	4-10	44-51	13-18	7-10	--	1-4	5-8	1-3	--	--	--	--
Palm Kernal	2-4	3-7	45-52	14-19	6-9	0-1	1-3	10-18	1-2	--	1-2	--	--
Palm	--	--	--	1-6	32-47	--	1-6	40-52	2-11	--	--	--	--
Safflower	--	--	--	--	5.2	--	2.2	76.3	16.2	--	--	--	--
Peanut	--	--	--	0.5	6-11	1-2	3-6	39-66	17-38	--	5-10	--	--
Cottonseed	--	--	--	0-3	17-23	--	1-3	23-41	34-55	--	--	2-3	--
Corn	--	--	--	0-2	8-10	1-2	1-4	30-50	34-56	--	--	0-2	--
Sunflower	--	--	--	--	6.0	--	4.2	18.7	69.3	0.3	1.4	--	--
Soybean	--	--	--	0.3	7-11	0-1	3-6	22-34	50-60	2-10	5-10	--	--
Rapeseed	--	--	--	--	2-5	0.2	1-2	10-15	10-20	5-10	.9	50-60	--
Linseed	--	--	--	0.2	5-9	--	0-1	9-29	8-29	45-67	--	--	--
Mustard	--	--	--	--	3.0	--	1.5	15-60	12	5-10	--	10-60	--

Table 2-1 Weight Percent of Fatty Acids in Various Fat and Oil Feedstocks

2.4 Biodiesel Manufacture

Biodiesel is a biodegradable fuel made in a chemical process where vegetable oil, recycled cooking grease and animal fats are combined with an alcohol to yield a monoalkyl ester (methyl ester). Ma and Hanna (1999) reviewed the production of biodiesel and transesterification is the most commonly used chemical process. The chemical processing takes place at mild conditions leading to lower capital startup costs. For example, the process of base-catalyzed transesterification is at low temperature (150°F) and low pressure (20 psi). Conversion is high and about 98 percent at these conditions. As depicted in the figure below, a fat or oil is reacted with an alcohol (like methanol) in the presence of a catalyst to produce glycerin and methyl esters or biodiesel. The methanol is charged in excess to assist in quick conversion and unconverted methanol is recycled. The catalyst is usually sodium or potassium hydroxide that has already been mixed with the methanol.

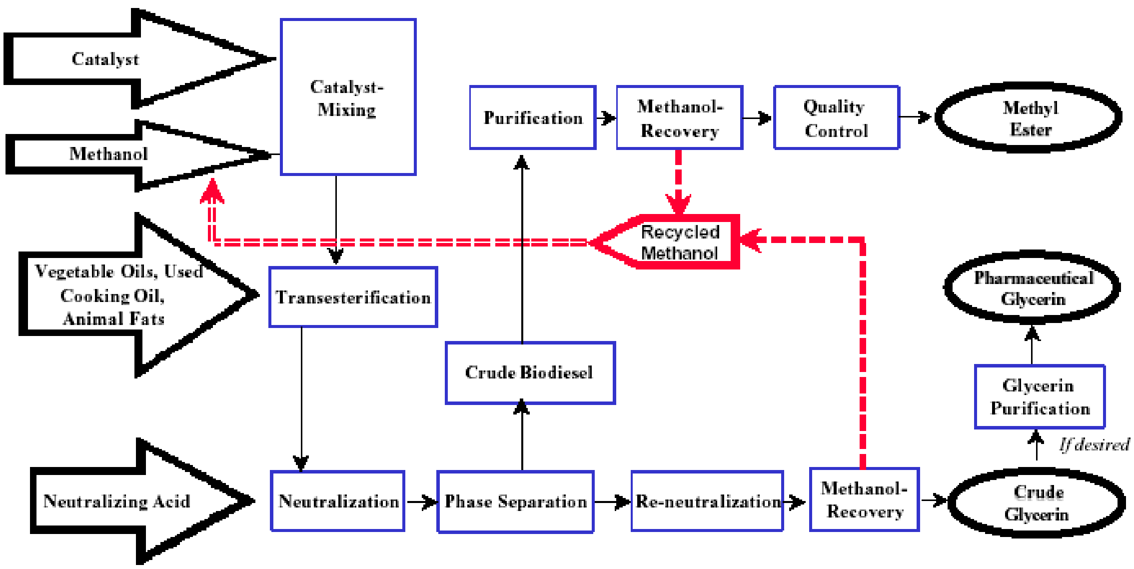

Figure2-2 Flow Chart of Biodiesel Production Steps

The heart of the biodiesel production is the chemical reaction of the vegetable or animal oil with alcohol as shown in Figure 2-3 below. Through the manufacturing process, 100 pounds of oil are converted into 100 pounds of biodiesel fuel and 10 pounds of glycerin.

CH_2OCOR'''			CH_2OH		$R'''COOR$
|		Catalyst	|		
CH_2OCOR''	+ 3 ROH	------>	CH_2OH	+	$R''COOR$
|			|		
CH_2OCOR'			CH_2OH		$R'COOR$
100 pounds Oil or Fat	10 pounds Alcohol (3)		10 pounds Glycerin		100 pounds Biodiesel (3)

Figure 2-3 Key Chemical Reactions in Biodiesel Production

According to the National Biodiesel Board (see www.biodiesel.org), the U.S. biodiesel industry production is rapidly increasing and there are 65 operating production plants in the United States. The annual production output for these plants was 75 million gallons in 2005, 250 million gallons in 2006 and 450 million gallons in 2007. Biodiesel plants continue to be built in great numbers, with capacity now well above 1 billion gallons. Overall, DOE estimates indicate that in total there is only enough feedstock to supply about 1.9 billion gallons of biodiesel per year (Alternative Fuels Data Center, 2005), representing approximately 5% of the on-road diesel used in the US.

2.5 Biodiesel Fuel Properties and Specifications

Fuel quality is very important to owners of diesel engines. Consumers expect all fuels to meet certain minimum quality, safety, and performance standards and engine manufacturers expect a fuel quality that does not affect engine performance and durability. Biodiesel fuel is no different and the minimum fuel quality specifications are defined in ASTM specification D6751, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels. ASTM represents the quality standard for the 100% biodiesel to be used in blending of biodiesel blends. The standard is independent of manufacturing process or feedstock and is designed to ensure that biodiesel has adequate quality for safe and satisfactory operation in a compression ignition engine. Similar to petroleum-based diesel specification (ASTM 975), the ASTM D 6751 specification starts with a workmanship statement: “The biodiesel fuel shall be visually free of undissolved water, sediment, and suspended matter”. Biodiesel should be clear and bright, although it may come in a variety of colors as color cannot be used as an indicator of predicting fuel quality. A portion of ASTM specification D6751 is shown in Table 2-2 and Appendix B provides further detail about ASTM –D6751. Please note the ASTM D 6751 in Appendix B is out of date as ASTM is in the process of issuing very important changes based on the discussions over the past several years and votes at their June 2008 meeting.

Property	Test Method[B]	Limits	Units
Flash point (closed cup)	D 93	130.0 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9–6.0[C]	mm^2/s
Sulfated ash	D 874	0.020 max	% mass
Sulfur[D]	D 5453	0.05 max	% mass
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report[E]	°C
Carbon residue[F]	D 4530	0.050 max	% mass
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	% mass
Total glycerin	D 6584	0.240	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered	D 1160	360 max	°C

Table 2-2 Selected Requirements for Biodiesel (B100) per ASTM D 6751

Issuance of the original ASTM D 6751 standards for biodiesel brought a level of credibility for this fledgling fuel but it was only the beginning of what was needed. There were still a number of issues and requirements for biodiesel to have the same credibility and acceptance as a fuel when compared with petroleum diesel fuel. For example, how to handle the different potential blend levels and other factors with the use of biodiesel fuel (Howell, 2006a). Fuel stability on use and storage was a contentious issue that was addressed in 2006. The ASTM members agreed to incorporate the same test used for oxidation stability for the biodiesel standard in Europe, namely the Rancimat standard method for oxidation stability (EN 14112). Cold flow properties were another area of concern and in June 2008 the ASTM committee adopted new standards and limits to deal with this issue for the B100. The June 2008 meetings also modified the petrodiesel specification ASTM D975 to include blends of up to 5 volume percent of biodiesel and created a new stand alone specification to handle bends of biodiesel up to 20 volume percent. ASTM members will continue to include new and improved methods, including different chromatographic methods (Porter, 2006, Cecil and Sidisky, 2006, Foglia, et al. 2006).

2.6 Properties of Commercial #2 Diesel and Biodiesel Fuels

Biodiesel differs from petroleum-based diesel fuel in a number of physical and chemical properties. Biodiesel has a specific gravity of 0.88 compared to 0.85 for diesel fuel, contains no nitrogen or aromatics and typically contains less than 15ppmw sulfur. Biodiesel contains 11% oxygen by weight, which accounts for its lower heating value and lower volumetric energy content. The energy content of biodiesel is roughly 10% less than diesel No. 2 and comparable to diesel No.1. Other comparative properties are shown in Table 2-3.

Fuel Property	Diesel	Biodiesel
Fuel Standard	ASTM D975	ASTM D6751
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower Heating Value, Btu/gal	~131,300	~117,000
Kin. Viscosity, @ 40°C	1.3-4.1	1.9-6.0
Specific Gravity kg/l @ 60°F	0.85	0.88
Density, lb/gal @ 15°C	7.079	7.328
Water and sediment, vol%	0.05 max	0.05 max
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. wt %	0	11
Sulfur, wt %*	0.05 max	0.0 - 0.0024
Boiling Point, °C	180-340	315-350
Flash Point, °C*	60-80	100-170
Cloud Point, °C	-15 to 5	-3 to 12
Pour Point, °C	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Stoichiometric Air/Fuel Ratio wt./wt.	15	13.8
Lubricity SLBOCLE, grams	2000-5000	>7,000
Lubricity HFRR, microns	300-600	<300

Table 2-3 Selected Properties of Typical Diesel and Soy-Derived Biodiesel Fuels.

The cetane number for biodiesel is generally higher than found in Federal diesel #2, but is comparable to that typically used in California. The cetane number for biodiesel depends on the feedstock used to produce the biodiesel. Cetane number increases for more highly saturated esters and for esters with longer chain lengths. Cetane number decreases with unsaturated content and the number of double bonds and as the double bonds and carbonyl groups move toward the center of the chain. Generally, higher cetane numbers are found for esters produced from tallow or yellow grease sources. Graboski and McCormick found that cetane numbers for soy-based biodiesel ranged from 45.8 to 56.9 with an average of 50.9.

One point of concern is that biodiesel has less favorable cold weather flow characteristics compared with convention diesel fuel. Some key properties in this regard are the cloud point and the pour point. The cloud point is the temperature at which wax formation can begin to plug the fuel filter. The pour point is a measure of the temperature at which the fuel is no longer pumpable. The cloud points of diesel #2 and Diesel #1 can range from -10 to +10°F and -40 to -60°F, respectively. Diesel #1 is often blended into diesel #2 in colder climates to produce more favorable cold flow specifications. The effects of biodiesel addition on the cloud and pour points for a petroleum diesel fuel are shown in Figure 2-4. Cold flow additives are available to mitigate these issues by inhibiting crystal formation, but they have varying degrees of success depending on the feedstock. NREL suggests that users specify to the blend supplier that the fuel remains crystal free at temperatures down to -14°F during the winter season. B20 has been used in cold temperature climates such as northern Minnesota and Wyoming, where temperatures regularly fall to below -30°F. Cold flow properties could be a limitation to the use of B100 in the wintertime.

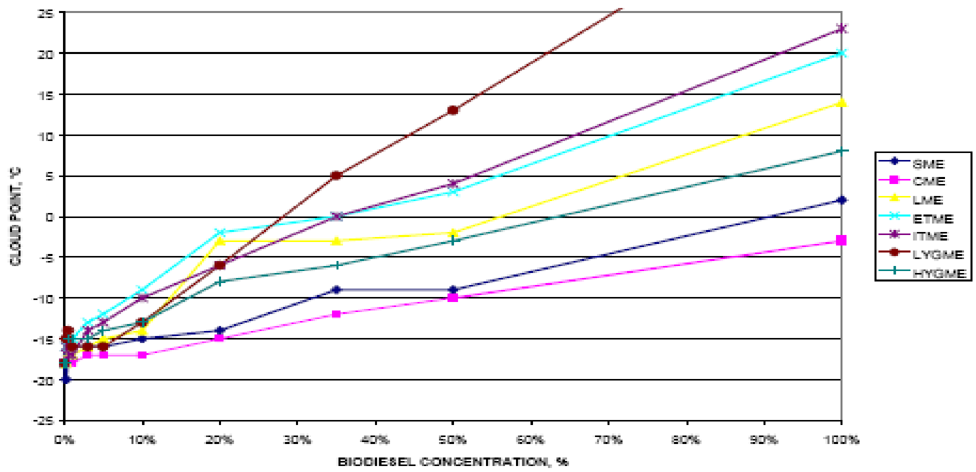

Figure 10. Biodiesel/diesel blend cloud point test results[11]

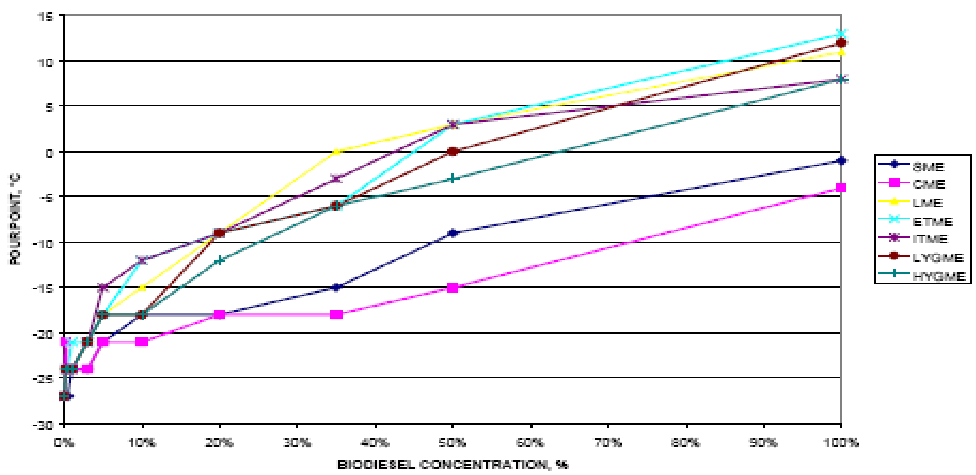

Figure 11. Biodiesel/diesel blend pour point test results

Figure 2-4. Effects of Biodiesel Addition on Cloud and Pour Points of Blends with #2 Diesel

Biodiesel has favorable properties for lubricity. Fuel lubricity is an important parameter since fuel pumps heavily rely on the fuel itself for lubricating many moving parts. The lubricity of biodiesel is higher than that of base diesel fuel. Even low levels blends of 1-2% biodiesel in petrodiesel can provide significant improvements in lubricity for a diesel fuel. There has been some discussion that low level biodiesel blends could be utilized in conjunction with the introduction of ultra-low sulfur diesel to improve lubricity, but these lubricity issues are largely being addressed by the petroleum industry through the use of additives. Biodiesel blends at the 2% level could be effective to provide adequate lubricity for fuels such as Fischer Tropsch diesel that have poor lubricity properties.

The flash point of biodiesel is also higher than that of typical diesel fuels. The flash point is a measure of the temperature to which the fuel must be heated to create a vapor/air mixture that can be ignited. This means that many safety precautions for handling diesel fuel would be more than adequate for handling biodiesel blends.

2.7 Biodiesel Blends with Petroleum Diesel

Regardless of starting materials, biodiesel always refers to a neat or pure fuel that meets the current Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, ASTM D-6751. However, biodiesel is usually blended with petroleum diesel and biodiesel blends or BXX refers to a fuel that is composed of XX volume percent biodiesel and diesel fuel. For example, B100 is neat or pure biodiesel and B20 is a blend of 20 volume percent biodiesel and 80 volume percent diesel fuels. The petroleum diesel fuel can be either a No. 1 or No. 2 meeting ASTM D-975, the standard for petroleum-based diesel fuel, or with JP-8.

When this project started there was no specification for biodiesel blends from B0 to B20 due to technical challenges from the automotive industry. A number of practical technical issues arose related specifically to biodiesel properties; such as low temperature properties, oxidative stability on storage and at high temperatures, microbial contamination and handling on distribution. For example, the cloud point of biodiesel is generally higher than petrodiesel and should be taken into consideration when blending. These issues are well covered in a report from the Department of Energy's National Renewable Energy Laboratory (NREL) [Tyson et al., 2004]. However, leading to the June 2008 ASTM meeting, a number of challenging issues were resolved and ASTM is expected to issue new specification in 2008 for neat biodiesel (ASTM D 6751), diesel blends with up to 5 volume percent of biodiesel (ASTM 975) and a new specification for blends from 5 to 20 volume percent biodiesel fuel.

2.8 Biodiesel Quality

The National Renewal Energy Laboratory (NREL) is the lead manager of the US biodiesel program and they have surveyed the quality and stability of biodiesel and biodiesel blends in the US, starting in 2004. Of the 27 B100 samples collected in 2004, 85% were found to meet all of the ASTM D6751 specifications (McCormick et al. 2005). Samples failing one requirement were often found to have an outlier or failing results for a second requirement. As a part of this study, oxidation stability tests were conducted using the Rancimat test which is used for the European biodiesel standard. The results showed that the typical biodiesel sample exhibited an induction of less than one hour on the test. The main factors affecting biodiesel stability are natural antioxidation content, polyunsaturated fatty ester content, and the level of mono and di-glycerides. This issue was resolved with the addition of the Rancimat specification to ASTM D6751.

A follow-up study fuel quality survey in 2006 showed more significant fuel quality problems (Alleman et al. 2007). Of the samples collected, the failure rate was found to be 59%. The primary failures were for total glycerin (33%) and flash point (30%). In the study, it was noted that even considering that the results apply only to the samples collected and was not based on a production volume, these researchers characterized these results as “alarming”. A follow-up study in 2007 found 90% of the B100 met specification, showing a significant quality improvement (Alleman 2008). This survey found that large producers and BQ-9000 producers readily met the specifications. Another fuel quality survey by NREL is planned for B100 during the 2009 timeframe. Taken as a whole, however, these results indicate that Caltrans should only utlize biodiesel from BQ9000 certified producers or distributors.

Some issues and concerns were identified with the proper blending of biodiesel to a nominal B20 or other level. Two options are available to produce blends of biodiesel with petroleum diesel, either in-line blending or splash-blending. In-line blending requires more expensive equipment so almost all biodiesel blends are manufactured using splash blending. This is a process where biodiesel and petrodiesel are sequentially added to the tank on a transport truck and completion of the mixing process to achieve uniformity in the blended fuel either occurs during the sequential addition of the fuels components to the tank or during the drive to the customer location (also know as stop-sign blending as the mixture will slosh from front to back of the tank as the delivery truck stops and starts.) As compared with in-line blending, there are fewer controls for the splash blending process but ethanol was added to gasoline for many years by this process without problems. The key issues are how the manufacturer mixes the denser biodiesel and the distance of driving to the customer’s tank. McCormick et al. (2005) found that 18 out of 50 samples of B20 collected nationwide were not nominally B20 (i.e., between 18 and 22% biodiesel), instead ranged from 7 to 98%. Foster et al. (2006) suggested that to alleviate this problem at the petroleum industry level, the petroleum diesel and biodiesel streams should be mixed by pumping them at the appropriate ratio of flow rates into a common pipe under turbulent conditions. This method is universally used in other refinery fuel blending operations to ensure accurate, homogeneous blends, such as blending fuel components at the refinery, additives at the refinery or terminal and today ethanol into gasoline at the terminal but are much more equipment and capital intensive. It is anticipated that these issues will be resolved as the biodiesel industry matures. A follow-up fuel survey of B20 blending is ongoing at this time that could provide confirmation of the improved blending capability (Alleman 2008).

Minnesota experienced quality problems with some biodiesel in the state not meeting D6751 specifications (Howell, 2006b). Minnesota was the first state to require diesel fuels sold in the state to be blended with 2% biodiesel. A number of issues were observed during the cold weather with fuel filter plugging and wax build-up on the filters of the test. As a result the vehicles ran poorly or stalled in cold conditions. The quality issues were traced to the biodiesel not meeting the specification for unreacted or partially reacted oils and fats (total glycerin). The program was temporarily halted from December 23, 2005 to February 10, 2006 and some enforcement measures were put into place including BQ-9000 like practices (described later), requiring a certificate of analysis for each batch of biodiesel sold, and fines/suspensions for producers making off-spec fuel. Since these measures were implemented, no further quality issues have been found since this program was reinstated. The petroleum industry is still emphasizing continuing development in looking at cold flow properties. Foster et al. (2006) noted some precipitation from biodiesel blends upon cooling was not detected using traditional wax tests and that some of the filter plugging occurred even with compliant B100. This issue was addressed in the June 2008 ASTM meeting and was added to the new ASTM D6751 specification. The point for Caltrans is that some districts have winter temperatures so the purchase specifications for both diesel and biodiesel fuels should include these low temperature tests.

Europe also put in place an extensive quality management system extending from the raw material to the final product supplied to the customer and a working group for biodiesel quality assurance is also in place for some countries. Reports of biodiesel not meeting the European specification are currently rare. Prior to the establishment of more rigorous procedures, Europe reportedly also had issues with biodiesel being out of specification for primarily oxidation stability.

The National Biodiesel Accreditation Program is a cooperative and voluntary program for the accreditation of producers and marketers of biodiesel fuel called BQ-9000. The program is a combination of the ASTM standard for biodiesel, ASTM D 6751, and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices. BQ-9000 helps companies improve their fuel testing and greatly reduce any chance of producing or distributing poor quality fuel. To receive accreditation, companies must pass a rigorous review and inspection of their quality control processes by an independent auditor. This ensures that quality control is fully implemented. BQ-9000 is open to any biodiesel manufacturer, marketer or distributor of biodiesel and biodiesel blends in the United States and Canada. A list of accredited producers and certified marketers can be found at www.bq-9000.org.

In addition to the formal D6751 specifications, some researchers have been working on simpler field tests that can be used to alert customers or operators of potential fuel problems that may require further action and analysis. Von Wedel (2006) discussed results from a field test indicator kit for B100. The test is designed as a quick check in the field for detecting traces of catalyst, mono/di/triglycerides, soaps, acids, and oxidized (aged) fuel. For the test, B100 is added to a ph indicator test vial, mixed by flipping and then allowed to settle into two phase with the fuel phase floating on top. The extraction of catalyst or acid from fuel to the aqueous pH indicator elicits color a visible color change. Soluble contaminants in the biodiesel can be extracted into the aqueous phase (fatty acid soaps) as visible turbidity, concentrated at the water-fuel interface (glycerides & fats, oxidized esters), and hydrated in the fuel as visible turbidity (mono, di, and triglycerides, fatty acids).

3 Literature Review of Biodiesel Users

3.1 Biodiesel Use in Compression Ignition Engines

The number of biodiesel users has grown with greater interest in low-carbon, renewable fuels. Further, the implementation of the tax credit has created a fuel on cost parity with petroleum diesel. A number of discussions on the use of biodiesel and biodiesel blends in compression ignition engines can be found in the Society of Engineers (SAE) meetings or the web pages of either the National Biodiesel Board (NBB)[2] or Engine Manufacturers Association ("EMA")[3]. In 2001, NBB prepared a report, *Biodiesel: On the Road to Fueling the Future,* which outlined the properties of biodiesel and the many applications where biodiesel was being successfully used. The NBB webpage contains both testimonial and as technical reports about biodiesel.

Perhaps more salient to consumers of biodiesel fuels are the views of the EMA, an international membership organization representing the interests of manufacturers of internal combustion engines. In 1995, EMA published a "Statement on the Use of Biodiesel Fuels for Mobile Applications." Their report was updated in February 2003 based on the increasing worldwide interest in reducing reliance on petroleum-based fuels and the potential to improve air quality with alternative fuels. The new EMA reports states that available data are limited and only for current engines and after control technologies. Their technical position statement provides a factual assessment of biodiesel fuels and the potential effects of their use with current technology engines. The statement was prepared as a resource for potential biodiesel fuel users, government, and the public. In its Technical Statement, the Association concludes:

- All biodiesel fuel should meet specifications approved by ASTM International or comparable European standards-setting organizations.
- Fuels blending up to 5% biodiesel with petroleum-based diesel fuel should not cause engine or fuel system problems.
- Biodiesel blends may require additives to improve storage stability and allow use in a wide range of temperatures. In addition, the conditions of seals, hoses, gaskets, and wire coatings should be monitored regularly when biodiesel fuels are used.
- There is limited information on the effect of pure biodiesel and biodiesel blends on engine durability during various environmental conditions.
- Biodiesel fuels reduce emissions of hydrocarbons and carbon monoxide but increase nitrogen oxide emissions when compared to petroleum-based diesel fuel. Neither pure biodiesel fuel nor biodiesel blends should be used as a means to improve air quality in ozone non-attainment areas.
- Individual engine manufacturers will determine the implications, if any, of the use of biodiesel fuels on their commercial engine warranties.

The EMA statements should be used as a checklist and guide for any fleet making a change from petrodiesel to biodiesel.

[2] National Biodiesel Board webpage is www.biodiesel.org
[3] Engine Manufacturer Association's webpage is www.enginemanufacturers.org

3.2 Engine Operation, Performance and Durability

The EMA made some technical observations about the differences in engine performance that owners should expect expected due to the differences in fuel properties. For example, the energy content of neat biodiesel fuel (B100) is about eleven percent (11%) lower than that of petroleum-based diesel fuel on a per gallon or volume basis, which results in a power loss in engine operation. However, the viscosity range of biodiesel fuel is higher than that of petroleum-based diesel fuel (1.9 – 6.0 centistokes versus 1.3 – 5.8 centistokes), which tends to reduce barrel/plunger leakage and thereby slightly improve injector efficiency. The net potential effect of using B100 is a loss of approximately five to seven percent (5-7%) in maximum power output and less than the 10% measured reduction in energy content. The actual power loss will vary depending on the percentage of biodiesel blended in the fuel and the operating cycle. EMA points out that adjusting the engine to compensate for power loss may violate EPA's anti-tampering rules and is not recommended.

Other EMA concerns that were less quantifiable included that neat biodiesel and higher percentage biodiesel blends can potentially lead to a variety of engine performance problems, including: fuel filter plugging, injector coking, piston ring sticking and breaking, elastomer seal swelling and hardening/cracking, and severe engine lubricant degradation. In addition, elastomer compatibility with biodiesel remains unclear; therefore, when biodiesel fuels are used, the condition of seals, hoses, gaskets, and wire coatings should be monitored regularly. EMA points out that information is limited on the effect of neat biodiesel and biodiesel blends on engine durability during various environmental conditions. EMA states more information is needed to assess the viability of using biodiesel over the mileage and operating periods typical of heavy-duty engines.

3.3 Statement of the Diesel Fuel Injector Manufacturers

During the period that EMA was investigating the available data for biodiesel, a consortium of diesel fuel injection equipment manufacturers ("FIE Manufacturers") issued a position statement[4] concluding that blends greater than B5 could cause reduced product service life and injection equipment failures. According to FIE Manufacturers, even if the B100 used in a blend meets one or more specifications, "the enhanced care and attention required to maintain the fuels in vehicle tanks may make for a high risk of noncompliance to the standard during use." As a result, the FIE Manufacturers disclaimed responsibility for any failures attributable to operating their products with fuels for which the products were not designed. Based on current understanding of biodiesel fuels and blending with petroleum based diesel fuel, EMA members expect that blends up to a maximum of B5 should not cause engine or fuel system problems, provided the B100 used in the blend meets the requirements of ASTM D 6751, DIN 51606, or EN 14214. If blends exceeding B5 are desired, vehicle owners and operators should consult their engine manufacturer regarding the implications of using such a fuel.

[4] See EMA webpage and Diesel Fuel Injection Equipment Manufacturers Common Position Statement on Fatty Acid Methyl Ester Fuels as a Replacement or Extender for Diesel Fuels (May 1, 1998).

3.4 Warranties

Warranty repair is a key decision element when purchasing a vehicle and a customer expects the fuel used in the truck will not affect the repair under warranty provision. While the EMA stated that manufacturers accept B5 for all engines, it also pointed out that individual engine manufacturers determine what implications, if any, the use of any fuel, including biodiesel, has on the manufacturers' commercial warranties. Some manufacturers indicate that proper fueling does not affect OEM's materials and workmanship warranties. In general, while the biodiesel supplier should warrant fuel quality, the use and effect on the customer's engine warranty needs to be understood by all parties: the biodiesel manufacturer/supplier, the engine manufacturer and the consumer/customer.

The international engine and automobile manufacturers have a prepared statement on the quality of fuels required to ensure optimal operation of the different vehicle and engine types they manufacturer. The draft Worldwide Fuel Charter (of August 2005) allowed the addition of biodiesel at up to 5% by volume to fuel categories 1-3 provided the biodiesel meets either ASTM D6751 or the European standard EN14214. Where biodiesel is used, it is recommended that pumps using biodiesel fuels should be marked. More recently, engine manufacturers have announced they will be working toward specification for use of blends up to B20 in their engines (NBB, 2006).

Engine manufacturers must provide a warranty for repair of the emissions control system for the lifetime specified in the Code of Federal regulations (40CFR85). A separate section, 40CFR86, specifies the test protocols, including petrodiesel fuel properties, required for engine certification. It is unclear what implications the use of biodiesel fuel has on emissions warranty, in-use liability, anti-tampering provisions, and the like. As previously noted, more information is needed on the impacts of long-term use of biodiesel on engine operations.

For construction equipment, Caterpillar is the predominant diesel engine supplier. For a number of the Caterpillar engines, biodiesel use up to 30% is approved, including many ACERT engine models, the 3406, 3126, and other models. For some models, biodiesel use only up to 5% is approved including 3003 through 3034, 3054, and 3056 engines. The biodiesel must meet the ASTM D 6751 specifications.

The following information is provided on Detroit Diesel's website[5] "Biodiesel fuels are alkyl esters of long chain fatty acids derived from renewable resources. Biodiesel fuels must meet ASTM Specification D 6751. Biodiesel meeting the D 6751 specifications can be blended up to 20% maximum by volume in diesel fuel. Failures attributed to the use of biodiesel will not be covered by Detroit Diesel product warranty."

Cummins also has a 6-page report on their web page[6]. An excerpt is shown below.

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[5] See Detroit Diesel web page at www.DDC.com :"*Engine Requirements — Lubricating Oil, Fuel And Filters,* 7SE270 0209 Copyright © 2002 Detroit Diesel Corporation

[6] See Cummins web page at www.cummins.com *Field Announcement, Subject: Cummins Position on the use of Biodiesel Fuel* –August 30, 2001

Warranty and the use of Biodiesel Fuel in Cummins Engines

Cummins neither approves or disapproves of the use of biodiesel fuel. Cummins is not in a position to evaluate the many variations of biodiesel fuels or other additives, and their long-term effects on performance, durability or emissions compliance of Cummins products. The use of biodiesel fuel does not affect Cummins Material and Workmanship warranty. Failures caused by the use of biodiesel fuels or other fuel additives are **NOT** defects of workmanship and/or material as supplied by Cummins, Inc and can **NOT** be compensated under the Cummins' warranty.

3.5 Biodiesel Stability

Fuel stability on storage and during use is a major industry issue for diesel and biodiesel fuels. Distillate fuels deteriorate due to complex oxidation and degradation reactions that occur when fuel is stored for long intervals or thermally stressed as in the fuel delivery system to a diesel engine. Oxidative stability refers to the potential of a fuel to undergo reactions with oxygen and thermal stability refers to the potential of a fuel to undergo reactions at the upper temperatures that might be encountered in the fueling process in an engine. In general, this mechanism refers to pyrolysis or coupling reactions that do not involve oxygen and which generate deposits. Both oxidative and thermal degradation lead to deposits that eventually become the sludge found in fuel tanks, fuel lines and fuel filters. In the field, these products can cause filter plugging, fuel line restriction, nozzle fouling and deterioration of fuel pumps and injector performance. Fuel composition and environmental factors directly influence the rate at which these processes proceed.

Processes leading to sediment formation for petroleum diesel and biodiesel differ substantially as compounds suspected of destabilizing the petroleum diesel fuel are not even found in biodiesel fuel. Petroleum diesel behaves more like a fossil fuel and biodiesel more like a vegetable oil. Instability of petroleum distillates is keyed to numerous heterocyclic compounds like indoles, pyroles, thiols and carbozoles. None of these compounds are in vegetable oils. Vegetable oils have a resistance to oxidation that depends on the degree of saturation, natural or added antioxidants and pro-oxidants and prior abuse. For vegetable oils, oxidation is slow until this resistance is overcome at which point the oxidation accelerates and becomes very rapid. Further, some work has shown that the sediments formed in biodiesel are soluble until the addition of petroleum diesel, again emphasizing the differences between the chemical nature, including polarity/solvency, of petroleum and biodiesel. A more exhaustive examination of the basic chemical reaction pathways and kinetics of lipid oxidation and autoxidation and thermal degradation in foods and biological systems is provided in Appendix D.

An oxidation stability test (the Rancimat, ASTM - EN 14112 method) was added to the D6751 biodiesel specification. In evaluating potential oxidation stability tests for biodiesel, several studies were conducted by NREL and the Coordinating Research Council (CRC). Accelerated oxidation stability tests involve stressing the biodiesel using a combination of elevated temperature, time, and enhanced oxygen exposure. Properties such as peroxide value, insolubles, evolution of volatile short chain acids, or heat of reaction are then measured to evaluate the effects of the oxidation. Some methods that were examined as possible methods for biodiesel include ASTM D2274 (oxidation stability of distillate fuel oil), ASTM D4625 (long term distillate fuel storage stability), ASTM D6468 (accelerated stability), AOCS Method 12b-92 (oil stability index or Rancimat test used in Europe), and others. Westbrook (2005) reviewed these and other methods and proposed that the Rancimat and a modified version of the D2274 would be the most appropriate for biodiesel. Another review of oxidation stability methods and biodiesel oxidation was also performed by Waynick (2005) as part of the CRC AVFL-2b program.

McCormick et al. reviewed oxidation stability of biodiesel and biodiesel blends as part of an their quality survey. They performed accelerated stability tests on 19 B100 samples and prepared a subset of 8 biodiesel blends for additional testing (McCormick et al., 2006a,b). The samples were tested for oxidation stability, thermal stability, gravimetric deposit formation, and measurements of iso-octane. Overall, they found that the stability of the biodiesel blends is dominated by the stability of the B100. A 3 hour Rancimat test for B100 appeared to be adequate to ensure stability of both B5 and B20 blends. They also found a correlation; samples with high total insolubles also had high iso-octane insolubles. Tests for this program include storage and handling, fuel tank testing, and aging in high temperature engine fuel system.

Given that in the normal fuel system there are accelerants that destabilize biodiesel fuel, the issue is how to control the pathways that cause sediments and harm to the engine. One approach is to use natural antioxidants that work with biodiesel such as TBHQ (t-butyl hydroquinone), Tenox 21, and tocopherol (Vitamin E), usually sold by food additive companies. Tenox is a mix of TBHQ as powdered antioxidants and is often difficult to mix into biodiesel. Canakci (1999) studied a number of blends of petroleum and biodiesel and used additives to stabilize the fuel. He found that TBHQ was effective for biodiesel and biodiesel blends. Williams Labs (1997) investigated oxidation and thermal stability for several biodiesel blends using ASTM 4625. They found some additives to be effective, but others were not. In general, the biodiesel blends were less stable than the neat fuels. TBHQ and Ethyl Hitec 4733 seemed to be the best additives. Waynick (2005) noted that TBHQ, pyrogallol (PY), and propyl gallate (PG), were the most effective antioxidants for fatty oils and esters.

While research continues in this area, DOE/NREL provided guidelines for conditions that will provide the highest levels of fuel stability for biodiesel (US DOE, 2006):

- The higher the level of unsaturation, the more likely the fuel will oxidize. As a rule, saturated fatty acids (such as 16:0 or 18:0) are stable. Each time the level of unsaturation increases (for example from 18:1 to 18:2 to 18:3) the stability of the fuel goes down by a factor of 10. So, a fuel composed primarily of C18:3 is 100 times more unstable than a fuel made of C18:1. Points of unsaturation on the biodiesel molecule can react with oxygen, forming peroxides that breakdown into acids, sediments, and gums.
- Heat and sunlight will accelerate the process, so it is best not to store B100 outside in clear totes in the summer.
- Certain metals such as copper, brass, bronze, lead, tin, and zinc accelerate the degradation process and form even higher levels of sediment than would be formed otherwise. B100 should not be stored for long periods of time in systems that contain metals. Metal chelating additives, which serve to de-activate these metals, may reduce or eliminate the negative impact of the presence of these metals. See also (National Biodiesel Board, 2002).

- Some types of feedstock processing and biodiesel processing can remove natural anti-oxidants, potentially lessening fuel stability. Vegetable oils and fats are produced with natural antioxidants – nature's way of protecting the oil from degradation over time. Bleaching, deodorizing, or distilling oils and fats, either before or as part of the biodiesel process can remove these natural antioxidants while other processes leave the antioxidants in the finished biodiesel.
- Keeping oxygen away from the fuel reduces or eliminates fuel oxidation and increases storage life. Commercially, this is done using a nitrogen blanket on fuel tanks or storing biodiesel in sealed drums or totes for smaller amounts of fuel.
- Antioxidants, whether natural or incorporated as an additive can significantly increase the storage life or stability of B100.

Studies show that in many commercial systems, the fuel turn over rate is in a range (two to four months) where fuel stability with B100 has not been problematic. The ASTM D4625 data suggests that the least stable B100 could be stored for up to 8 months, while the most stable could be stored for a year or more. The National Biodiesel Board recommends a six month storage life for B100.

Often large tanks of product are filtered with a water coalescing filter and a particle filter. Water removal rates for fuel filters are typically a 95% minimum. SwRI conducted a study to look at different fuel filters and biodiesel blends (Besse, 2006) and found that water separation characteristics vary as a function of type of biodiesel blend, filter media type, and flow rate. The biodiesel fuel blends typically had lower interfacial tension (IFT) values than the diesel, with rapeseed biodiesel blends showing better water removal characteristics than the other biodiesels tested (soy-biodiesel and yellow-grease biodiesel) over the limited test matrix used. The researchers note that other data, however, has shown lower water removal characteristics for rapeseed biodiesel. Overall, their research indicates potential water separation problems with B5, regardless of filter type. Tondreau (2006) of Davco also examined fuel filtration with biodiesel and ULSD and suggested that using B20 blends could jeopardize water separation.

3.6 Biodiesel Solvency & Filter Plugging

Several studies have been undertaken to better understand if there might be any negative impact of biodiesel on system durability. The primary issues for biodiesel use are its effect as a solvent and material compatibility with elastomers, plastics, seals, etc. The building blocks of biodiesel, methyl esters, are commonly used in solvent products and cleaners. When using biodiesel, there is some tendency for it to dissolve accumulated sediments in diesel storage tanks and engine fuel tanks. These dissolved sediments travel through the system and lead to clogged fuel filters. In some cases, injector deposits or injector failure could occur, but this is a rare occurrence. Most users of B20 typically do not clean their fuel tanks prior to use since B20 is sufficiently diluted to mute the solvent effect. It is suggested that extra fuel filters be maintained on hand during initial use, since cases of filter plugging have been reported and are more likely in the first few tanks. The effects of B100 would be greater so it is suggested that fuel tanks be cleaned and extra precautions be taken with the fuel system for B100 use.

3.7 Elastomer Durability

Biodiesel can also cause degradation, softening, or seeping through some hoses, gaskets, seals, elastomers, glues, and plastics with prolonged exposure. Concern about elastomer degradation is more critical for applications where B100 is used as opposed to B20. Nitrile rubber compounds, polypropylene, polyvinyl, and Tygon are particularly vulnerable to B100. Materials such as Teflon, Viton, fluorinated plastics, and Nylon, on the other hand, are compatible with biodiesel. Older vehicles manufactured before approximately 1993 are more likely to contain materials that could be affected by B100 over longer periods of time. Engine newer than 1993 and modern repair kits may contain biodiesel compatible materials, but not always. For use at more standard B20 blend levels, fleet experience has shown that material compatibility issues are minimal, even for elastomers made of materials such as nitrile rubber that are not compatible with higher biodiesel blends.

Frame and McCormick (2005) conducted a set of tests of evaluate the compatibility of elastomers with biodiesel and ethanol diesel blends. For this test, six different elastomers were soaked in a certification diesel fuel, a 15% ethanol blend, and a B20 blend for 500 hours at 40C. The elastomers were subsequently examined for thickness, diameter, and break load before and after being soaked in the fuels. The elastomers soaked in the B20 blend did not show any significant differences from those soaked in the diesel fuel, and it was concluded that all the tested elastomers were compatible with B20. Some effects were observed for the ethanol blends, hence, it was concluded that these elastomers may not be fully compatible with all application for ethanol blends.

The Associated Octel Company Limited of the United Kingdom (2005) conducted several tests on biodiesel blends to evaluate system durability as part of the CRC-2a program. This includes elastomer immersion tests, injector wear tests and fuel pump wear tests with B5 and B20 blends, including some highly oxidized blends. The elastomer immersion tests showed that fluorocarbon elastomers of medium to high fluorine content were the most compatible with the biodiesel blends. Some of the other candidate materials showed generally good resistance to changes in physical properties but exceeded the typical acceptable levels of degradation in one or more tests. The injector and fuel pump wear tests for the highly oxidized B20 blend had to be cut short due to filter blockage. The injector wear tests for the other candidate blends indicated that the lubricity of the test fuels were adequate for protection over the 500 hour test period. The fuel pump lubricity tests also indicated that all fuels were within the normal range expected for commercial diesel fuels over a 500 hour test period. Test on a common rail test rig also showed that the test fuels provided adequate lubricity.

In an earlier 1997 study (Williams Labs, 1997b), a series of fuel pump tests were conducted on two B20 blend. One of the blend was made with an on-spec B100, while the other sample exceeded the limits on the acid specification. The tests with the on-spec B20 showed no problems. The test with the off-spec B20 had problems with pressure drops across the filters and deposits. The authors indicated that these issues could be attributed to the high acid value, although Waynick (2006) in a subsequent review indicated that differences in the total glycerin may have contributed to the observations.

Some injector tests were performed with a Cummins L-10 injector using three B20 blends, a B100, and three diesel fuels (Stavinoha). The test results showed that while the average flow loss was never a problem for any of the fuels, the visual deposit rating of the injectors showed that each B20 fuel was significantly worse than either the B100 or the corresponding petroleum diesel.

Several engine durability tests have been conducted over the years on biodiesel, although data in this area is still limited. The National Biodiesel Board conducted two 1,000 durability studies in the mid-1990s. One was conducted on a B20 soy-biodiesel blend and a 6V-92TA DDC engine (Fosseen, 1995). Several problems were noted in this study including deterioration of fuel injectors, serious ring damage, and problems with fuel atomization. The authors speculated that the B20 may not have been the cause of these issues, although this was based on similarities of the B20 and regular diesel in viscosity, heat output, and specific gravity. The other study used a B20 soy-based biodiesel with a Cummins N14 engine (Tao, 1995). This test was terminated after only 650 hours due to fuel pump deposits, filter plugging, and early pump failure. The deposits included fatty acid esters in their composition.

Peterson et al. (1999) conducted a 1000 hour engine durability test using blends of a hydrogenated soy-ethyl ester on a 3 cylinder diesel engine. They did observe some filter plugging during the winter months for the biodiesel blends. They concluded that cold weather operation required heating for the fuel tanks and fuel filters. The engine operated on the biodiesel blend showed equal or reduced wear metals and was much cleaner internally when operated on 100% biodiesel. Perkins et al. (1991) did a 1,000 hour engine test with three identical engines powered by 100% rapeseed methyl ester (RME) biodiesel, B50, and straight diesel. RME use was similar to that of D2 for engine performance, analysis of concentration of wear metals in the lubricating oil, and injector deposits. Zhang et al. conducted additional tests on these engines and fuels over a 200 hour test. They found a slight decrease in power for the neat RME, but no significant differences in engine wear. Fuel dilution was also noted, but only during the first 50 hours of the test. Ali and Hanna (1996) conducted a 200 hour engine test on a Cummins N14-410 using a blend of 13% beef tallow, 7% ethanol, and 80% diesel. The engine suffered some injection failures during the test, but these were traced back to cracks in the injector tips due to improper installation.

3.8 Fleet Operations

The use of biodiesel has increased considerably in recent years and there is a growing body of data on the use of biodiesel in fleet or vehicle applications. Still, the information available on fleet operations in the open literature is more limited. The National Renewable Energy Laboratory surveyed and compiled biodiesel demonstration projects that were conducted between 1992 and 1997 (Tyson, 1998). This included demonstrations in a steamboat on the Ohio River, a bus at the 1996 Atlanta Olympic Games, and a work boat in Virginia.

Several studies conducted over the course of the 1990s showed no unusual effects for the use of biodiesel fuel in vehicles/fleets. The Ohio Department of Transportation used B20 in five dump trucks/snow plows (Malcosky and Wald, 1997). The focus of the study was on maintaining fuel quality and a total of 60,000 miles of B20 operation was accumulated. A two year trial was conducted in Minnesota on road maintenance vehicles using B20 (Bickel and Strebig, 2000). The vehicles utilized 25,000 gallons of B20 and operated for approximately 135,000 miles. The B20 use showed no adverse effects on fuel economy, no deposits or wear in the fuel system, and the oil analysis showed no unusual engine wear for fuel dilution.

The University of Idaho conducted several demonstrations in conjunction with various partners. Taberski et al. (1999) demonstrated a Dodge pick-up truck for over 90,000 miles in Yellowstone National Park running on 100% Canola ethyl ester. Oil analyses, compression, injector tests, and engine and fuel pump teardown inspections did not show any excessive wear or deterioration as a result of using the biodiesel. Peterson et al. (1999a) tested a 1992 Dodge pick-up with an on-board B20 mixing system for over 100,000 miles. The pick-ups fuel filter was changed 13 times over the four year test due to filter plugging and associated power loss. To help prevent rust formation and filter plugging, the fuel and mixing tanks were changed from mild to stainless steel. Peterson et al. (1999b) conducted a 100,000 miles demonstration on a 1994 Dodge pick-up. An extensive 200,000 mile road test on B50 was conducted with a Kenworth class 8 truck equipped with a Caterpillar 3406 engine was conducted as part of the Pacific Northwest and Alaska Regional Bioenergy Program with several partners (Chase et al., 2000). An extensive engine inspection and analysis at the conclusion of the demonstration showed no excessive wear and no injector degradation.

In Europe, as part of the “Stability of Biodiesel” (BIOSTAB) (2003) a 19 month, four vehicle fleet was run was made with a B5 made from used frying oil. Over 40,000 miles of operation was accumulation with the B5 fuel. The engine lubricant, fuel delivery system, and fuel storage system did not show any significant deterioration. Some problems were report with the oxidation stability of the bottom layers of the storage vessel significantly exceeding the EN 590 limits.

NREL evaluated a fleet of 9 buses from the Regional Transportation District of Denver over a period of 2 years (Proc et al., 2005, Proc, 2006). The buses were 2000 Orion Vs equipped with Cummins ISM engines. Five of the buses were operated on B20 while the other 4 were operated on regular petroleum diesel and each bus accumulated approximately 100,000 miles over the same bus route. The in-use data showed no difference in the average fuel economy, although laboratory testing showed a 2% reduction in fuel economy for the B20 vehicles. Engine and fuel system related maintenance costs were nearly identification between the two groups with the exception of repairs needed during the final month on one of the B20 buses. There were some problems with fuel filter plugging, which was likely caused by out of specification biodiesel, although the exact cause was not determined. The actual biodiesel levels in the delivered loads showed an erratically varying biodiesel content. The fuel samples collected from the vehicles, on the other hand, were near or at B20 indicating a more complete blending occurred during delivery and in offloading of the fuel. Oil analyses indicated no additional wear metals and significantly lower soot levels from the use of B20.

NREL is also working with the St. Louis Metro on an in-use evaluation of biodiesel in their transit buses (Proc, 2006). The study includes 15 2002 Gillig Phantom buses with Cummins ISM engines, with 8 operating on B20 and 7 operating on ULSD. The buses were monitored for a period of one year from October 2006 to September 2007 initially. Throughout the operation period, documentation was collected for vehicle performance and operation (mileage accumulation, fuel use, maintenance costs) and subsequently analyzed. The possibility of additional years of operation is contingent upon fleet approval and funding.

Humber et al. (2004) conducted a survey of biodiesel fleet use in different states. They found at that time that 31 states were either actively considering, using or had tested biodiesel blends in or for their fleets. Nineteen states reported program experience with the use or testing of biodiesel in their fleet operations. A number of the states report increases in filter plugging with the biodiesel use, although all of the states indicated the problems were resolved when the filters were replaced. Problems with using biodiesel in cold weather were not found to be widespread, although Iowa and Ohio did report filter plugging during cold weather periods.

Biodiesel has been used extensively by the US Postal Service (USPS), with usage near the 1,000,000 gallon level per year during 2003 and 2004. In 2004, 929 USPS cargo vans, truck tractors, spotter tractors, and step were using B20. The USPS removed engines and fuel systems from 8 vehicles that were operated on biodiesel, including four 1993 cargo vans and four 1996 Mack tractors (Fraer et al., 2005). The engines represented 4 years and more than 600,000 miles of use on B20. The engines and fuel system components were disassembled, inspected, and evaluated. The results indicated little differences between the operational and maintenance costs for the B20 and petroleum fueled groups and no differences in wear or other issues were noted during engine teardown. The Mack tractors did have a higher frequency of fuel filter and injector nozzle replacement, as well as some sludge build-up on the rocker arms. Similar observations were not found for the Ford vehicles, which could be related to the smaller volume of fuel circulated in these smaller engines. Additional work was done with the USPS with a new cargo van evaluation over a one year comparison for fuel economy and maintenance (Proc, 2006)

The military is the largest user of biodiesel in the United States. One B20 demonstration was conducted at Scott Air Force Base in Illinois (Kearny and Benton, 2002). No filter plugging or other operational problems were reported during this demonstration. Fuel quality was monitored throughout the study, and several loads of B20 exceeded the military limit on solids content, with many containing visible solids.

In 2002, the Kentucky Division of Energy provided grant funding to offset the incremental cost of biodiesel for several school districts (Clean Cities News, 2004a). Six school systems utilized signed up to utilize the fuel with blend levels of B2 or B20. A total of 300 buses in this project used B20 and 50 used B2. The fuel was supplied by in state suppliers, Griffin Industries for the yellow grease and the Kentucky Soybean Board for the soy-based biodiesel. The cost differential for the B20 is approximately \$0.15 to \$0.20 more for B20 than regular diesel.

In Las Vegas, the Clark County School District operated nearly all of its buses on B20 (Clean Cities News, 2004b). The school district began with a small pilot project in 2001. Beginning with the 2002-2003 school year, the school district began running almost all of its 1,140 buses on biodiesel. The biodiesel is supplied by Biodiesel Industries, which utilizes locally obtained restaurant grease from the hotel-casino industry. A user survey from the Las Vegas Clean Cities is included under section 4.

4 Task 1 Review of Specifications, Cost, Handling and Regulation

Task 1 was directed to a Literature and Field Application Review. A significant portion of that review is included in Chapters 2 and 3 related to fuel manufacture, equipment compatibility and warranty. Chapter 4 provides more focused review and analysis for specific areas of biodiesel use including fuel specification, availability, cost, petroleum displacement, emissions and regulation.

4.1 Task 1.1 Fuel Specifications

Deliverable: UCR will conduct a comprehensive evaluation of the specifications used for biodiesel and biodiesel blends.

At the time of the proposal, biodiesel was widely used; however, there was no recognized fuel specification by either the fuels division at the California Air Resources Board (CARB) or the consumer protection offered via the CA Weights and Measures Group, the two groups responsible for fuels specifications in California. As a consequence, UCR offered to work with the military, the EMA and the ASTM committee members to provide Caltrans with the latest information for developing a specification for Caltrans. The military is the largest user of biodiesel fuel in the United States and had the most experience in writing specifications and using the biodiesel fuel. In addition, contacts with the EMA offered direct information on their concerns based on product design and information they were obtaining from the field experience. EMA information would be useful for learning more about blend levels approved for warranty compliance. UCR kept its pulse on the direction of the future ASTM specifications by attending, as invited participants, the meetings held on the national technical roadmap for biodiesel.

As mentioned earlier, the most significant changes were from the June 20008 ASTM meeting where they announced:

- Changes to the existing B100 biodiesel blend stock specification (ASTM D6751)
- Finished specifications to include up to 5% biodiesel (B5) in the conventional petrodiesel specification (ASTM D975)
- A new specification for blends of between 6 percent biodiesel (B6) to 20 percent biodiesel (B20) for on and off road diesel.

After the demonstration testing went well at the Caltrans District 8 facility in Indio, as discussed below, Caltrans worked with UCR to draft a B20 specification for the widespread introduction of biodiesel fuel and its blends. Based on the military specification (Appendix E) Caltrans developed the original specification and DGS made some refinements (Appendix F). The latest statewide bulk fuel contact released by DGS includes specifications for B5 and B20 and the language incorporated in the latest ASTM standards: D975, D6751, and D7467. UCR noted that current Caltrans purchases follow ASTM D975 and only have the fuel supplier measure the low temperature properties. UCR has recommended that the Department of General Services (DGS) purchase specifications for both diesel and B20 state that these fuels "shall meet the cloud point limits specified in ASTM section X4 in D975" and that the cloud point is measured and reported.

4.2 Task 1.2 Fuel Storage and Handling

Deliverable: UCR will evaluate issues related to the storage and handling of biodiesel.

The literature was reviewed on issues such as the oxidation stability of biodiesel, cold weather performance, and chemical additives to improve performance. Recommendations are provided on any special storage requirements for biodiesel or biodiesel blends. Recommendations are also provided for use of biodiesel under cold weather conditions. The use of additives to improve characteristics of biodiesel blends was also included in any recommendations.

Some of the information was reviewed in Chapter 2 and the most useful information can be found in the NREL Document entitled “Handling and Use Document.” In addition the NBB issued a check list of recommended best practices that should be reviewed before converting to B20. That information is provided in Appendix G.

4.3 Task 1.3 Pricing and Availability

Deliverable: UCR will survey suppliers of biodiesel to determine the price and availability of biodiesel throughout the state.

The survey will include information about the base feedstock material used for each of the marketed biodiesels. Estimates of the potential expansion of the biodiesel market will be obtained based on contacts with NREL, the NBB, and the open literature. Regulations pertaining to biodiesel tax credits and EPAct credits and their impact on costs will also be reviewed.

4.3.1 Biodiesel Price and Supply

The market price of biodiesel varies on a daily basis just like other fuels prices. The chart, Figure 4-1, lays out the cost of the various steps associated with the manufacture and delivery of biodiesel fuels. The cost is Figure 4-1 includes the Federal Tax Credit of up to $1/gallon Looking at each of the parameters, it is clear that the primary driver affecting the overall cost of producing and delivering biodiesel fuel is the feedstock cost. The percentage of each activity cost was estimated based on the cost of fuel in August, 2008.

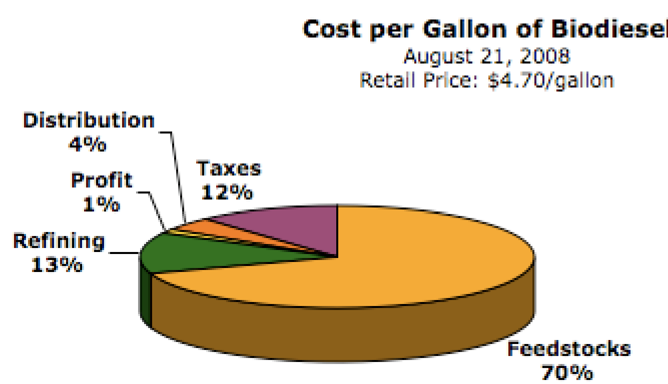


Figure 4-1 Cost per Gallon of Biodiesel

Refining - Cost of manufacturing biodiesel using the transesterification process.

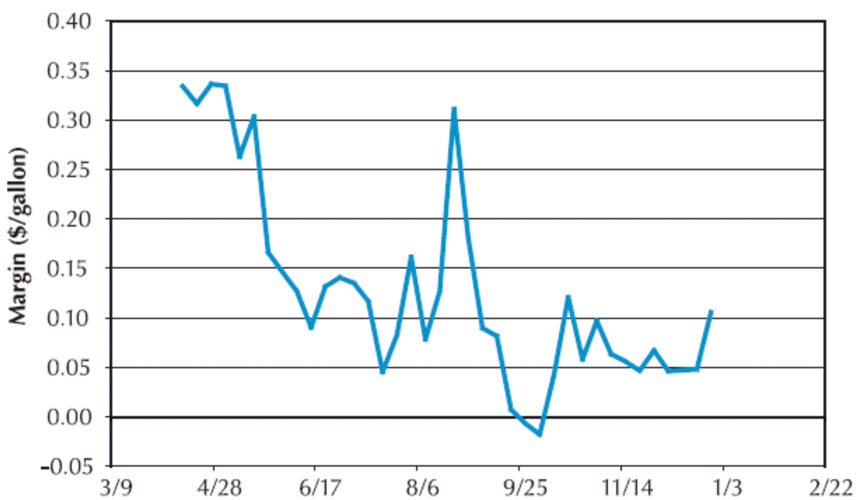
Distribution - Cost to deliver fuel to the B100 Community Trail, maintain equipment, and administer transactions.

Taxes - Federal and state taxes applied to biodiesel.

Feedstock cost is the primary driver for the delivered price of biodiesel. The percentage on Figure 4-1 represents those costs for raw materials including chicken fat, methanol, catalyst, filter aids and yield adjustment; minus the federal blender's tax credit ($1.00/gallon for virgin fats and oils and $0.50/gallon for recycled fats and oils). These costs represent 70% of the overall delivered price.

DOE's Energy Information Administration (EIA) uses a process-costing approach to model the impacts of net feedstock production costs plus capital and operating costs. The feedstock cost of the oil or grease is the largest single component of biodiesel production costs. Yellow grease is much less expensive, about 50%, of the cost of soybean oil, but its supply is limited, and it has uses other than fuel. For example, yellow grease is used as an animal feed additive and in the production of soaps and detergents.

Biodiesel Supply Biodiesel plants will not be built unless investors expect to receive a competitive return on their investment. Before a biodiesel plant can begin to pay out a return on investment, the plant must generate positive operating margins, which are defined as revenue minus all operating costs, including labor, energy, and feedstock costs. In 2007, most U.S. biodiesel plants found that they could not cover their operating expenses. Thus, actual production in 2007 was less than 500 million gallons, far less than the 1.85 billion gallons in capacity.



Source: Soybean oil and biodiesel weekly prices for Iowa from the Agricultural Marketing Service, U.S. Department of Agriculture.

Figure 4-2 Average Returns over Operating Cost for an Iowa Biodiesel Plant

In addition to the federal tax credits for biodiesel production, the USDA has offered grants through the Commodity Credit Corporation (CCC) for past several years to encourage biodiesel production. The CCC payments for expansion of biodiesel production in the fiscal years 2004-06 are $1.45-$1.47 (2002 dollars) per gallon for soybean oil biodiesel and 89-91 cents per gallon for yellow grease biodiesel. Base production payments apply to production up to the level of the prior fiscal year, and additional production payments are for production above the level of the prior fiscal year. The CCC payments effectively reduce the variable cost of additional soybean oil and yellow grease biodiesel to $1.10 and 53 cents per gallon, respectively, in fiscal year 2004. Additional units produced in fiscal year 2004, however, become base units in fiscal year 2005 and are eligible only for much smaller, and declining, base production payments. The variable cost of soybean oil and yellow grease biodiesel added in fiscal year 2004 jumps to $2.32 and $1.27 per gallon, respectively, in fiscal year 2005.

The transportation bill passed by the Senate on February 12, 2004, included excise tax credits for biodiesel blending that have been continued in subsequent legislation. The legislation allows diesel blenders to claim a credit against the applicable Federal motor fuels excise tax if a batch of diesel fuel contains biodiesel. If the blender uses biodiesel made from virgin oil, such as soybean oil, the credit is $1 (nominal dollars) per gallon of biodiesel. If the blender uses biodiesel made from non-virgin oil, such as yellow grease, the credit is 50 cents per gallon of biodiesel. The legislation also included business income tax credits at the same rates for the blending of biodiesel from virgin or non-virgin oil.

4.4 Task 1.5 Regulatory Elements

UCR will evaluate regulations on a state and federal level pertaining to biodiesel and biodiesel use. This will include regulations dealing with tax credits, as well as those dealing with biodiesel specifications, emissions requirements, or limitations on the sale of biodiesel.

The most significant action was the passage of the $1 per gallon federal tax credit for biodiesel fuels and that was covered in the prior section. This tax credit could be viewed as a feedstock cost reduction so the product is more cost competitive with petroleum diesel. In any case, it was intended to increase the production of biodiesel and that is what happened.

A significant action on specifications is expected in California now that the ASTM has issued a specification for B20. California weights and measures laws and regulations are the responsibility of the Division of Measurement Standards (DMS). The DMS group relies on ASTM specifications for enforcement in the stare. Now with specifications for B0-B5 and for B20, we can expect California standard specifications for these fuels.

Emission requirements for California are still a dilemma and the California Air Resources Board is carrying out a major research program (>$1 million in funding) with the UCR to answer questions for the state. The next section covers what is known about emissions.

5 Task 1.4 Emissions Impacts

5.1 Introduction

Deliverable: A comprehensive evaluation of the literature pertaining to the emissions benefits/debits of biodiesel will be performed.

This will include general biodiesel emissions data compiled by industry, government and in peer reviewed literature. The literature review will also emphasize studies more relevant to Caltrans, including those related to off-road equipment and engines and those utilizing fuels meeting California specifications. A model being developed under an ongoing Caltrans study will also be expanded to incorporate the emissions effects and petroleum displacement of biodiesel in the Caltrans fleet. This model is still under development and will be incorporated into a follow-up phase for this program with Caltrans. Based on information gathered in this subtask, a determination will be made as to whether additional in field emissions tests will be needed.

5.2 Background

The emissions of vehicles and construction equipment can be affected by a number of different factors including engine technology, engine age, driving or operating mode, as well as fuel type. While the focus of this section is on fuel effects, it is important to understand all of these factors can play a role in the emissions generated for a specific comparison tests. Work by Clark et al. (2002) puts the importance of various parameters involved in determining emission factors for diesel engines into the proper perspective. Their research considered: vehicle class and weight, driving cycle, vehicle vocation, fuel type, exhaust after treatment, vehicle age, and the terrain traveled. The parameter that most heavily affected emissions was the driving cycle as variations changed the PM and NO_x emissions by factors of 15 and 3, respectively. Clark's results are shown in Figure 5-1.

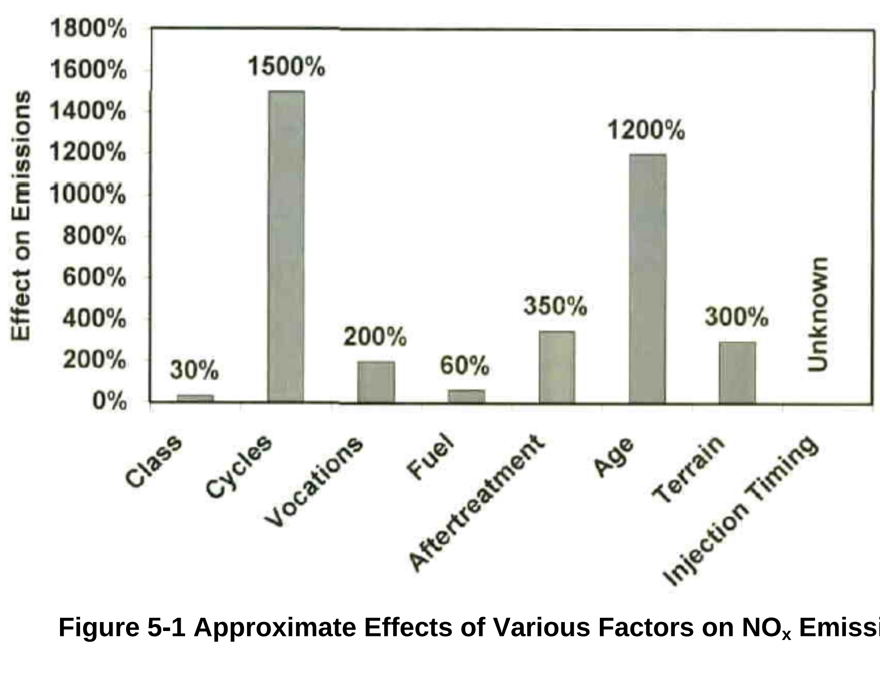


Figure 5-1 Approximate Effects of Various Factors on NO_x Emissions

An important and relevant observation is the small effect that fuel properties have on the emissions as compared with other factors, especially the test cycle or the age of the vehicle.

5.3 Effect of Diesel Fuel Properties on Emissions

Miller (2003) reviewed the effect of diesel fuel properties on emissions as part of the review process for the implementation of a new diesel fuel in California. Two points were expounded in that work. First, changes in diesel fuel composition and properties can affect emissions levels, and second, the effects of the change on each fuel property cannot be easily understood because of the complex interactions between engine operating conditions and fuel properties. Studies of fuel variables are further complicated by the fact that the properties tend to be intercorrelated in the test fuels. For example, fuels with a high density often have a high content of aromatics.

Lange (1991) studied diesel fuel properties in DDC Series 60 and concluded that the fuel density rather than aromatics was the dominant factor for PM emissions as the more dense fuels led to over fueling of the engine. A follow-on study by Den Ouden et al. (1994) considered fuel effects and PM emissions for several engines. He reported that three of the five heavy-duty engines showed a cetane effect on PM and density effects were second order in a steady-state cycle. Density effects were found for the transient cycles, however. Ullman and Human (1991) reported that engine tuning was more important that fuel properties; and lower emissions were favored with a fuel that had lower aromatic and sulfur contents and high cetane number.

Crowley et al. (1993) reported that sulfur, density and cetane had the most effect on PM emissions and that total aromatics had no affect. It should be noted that in these earlier studies, fuel sulfur levels much higher than those used in ultra low sulfur diesel were typically tested. However, Rosenthal and Bendinksy (1993) determined that the aromatic content is the primary fuel parameter driving NO_x and PM for engines operating below 1994 emission levels. Signer et al. (1996) reports on a very large industry study, the European Programme on Emissions, Fuels and Engine Technologies (EPEFE). Their results show that NO_x emissions increase with increased timing and polyaromatics and the degree of emissions increase depends on the engine. They concluded that fuel density was the most influential property to reduce NO_x.

Stradling et al. (1997) reported on the influence of fuel properties and injection timing on emissions. His findings show that the NO_x emissions could be controlled by injection timing, fuel density and aromatics content. Lee et al.'s (1998) review points out that decreasing aromatics resulted in a small benefit in NO_x emissions. They also commented that one study operated in an "off-design" mode did not show an aromatic effect until it was operated in a more optimal timing regime. Lange et al. (1997) investigated fuel properties on advanced engine technologies and concluded that the fuel effect for cetane and NO_x emissions was dependent on the test cycle and the interaction between engine design and the ignition properties of the fuel. Mason et al. (2000) reports on the results of the EPA's heavy-duty engine working group (HDEWG). They found that NO_x emissions correlated with density, cetane, and mono- and poly-aromatics.

Considering these careful research studies and many others, it should be apparent that there is still not a clear understanding of the exact relationships between diesel fuel composition, engine operation and emissions; even though that subject has been studied extensively for many years. While fuel effects can be related to a number of factors, Mann et al. (1998) pointed us in another direction by stating that fuel effects can change the engine operating conditions and emissions, a factor that may be important for biodiesel.

The emissions of biodiesel and biodiesel blends have been studied extensively over the years. This includes engine dynamometer studies, chassis dynamometer studies and other type of studies. It is important, however, to understand in a broader context how the studies may apply directly to Caltrans applications where in-use conditions for off-road equipment may differ from those obtained in engine dynamometer test stands. Also, comparisons with California fuels are important, since California fuels meet more stringent regulations than those applied to standard EPA No. 2 diesel blends.

5.4 EPA's Report on Changes to Emissions Using Biodiesel Fuel

In October 2002, the United States Environmental Protection Agency (EPA) published their draft Technical Report, *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions.* The EPA report is the most comprehensive government review of the emissions from diesel engines using neat biodiesel and biodiesel blends with petrodiesel and was prepared in response to increased:

- Use of biodiesel in heavy duty fleets due to EPAct changes,
- Interest in developing appropriate emission factors for biodiesel,
- Appeal for biodiesel to address energy supply issues, and
- Lobbying by the biodiesel industry for favorable tax legislation and blending mandates.

The EPA published its draft and presented their findings along with comments from others at the Mobile Source Technical Review Subcommittee to the Federal Advisory Committee on Clean Air (FACA) on October 16, 2002. Reports from the EPA and various stakeholders were presented at the meeting and can be found on the EPA website. EPA's report was to provide information to interested parties who may be evaluating the appropriateness of the use of biodiesel and the potential air emission impacts of biodiesel. EPA intended to provide a comprehensive analysis of exhaust emission impacts of biodiesel use at any concentration for regulated and unregulated pollutants.

EPA's approach was to collect all publicly available emissions data from various emissions test programs into a single large database (39 studies) and then use statistical regression analysis methods to correlate biodiesel concentration with emissions. They assumed engines and base fuels were random variables and made adjustments or eliminated data for the reasons defined in their report. Most of the effort was directed to heavy-duty engine data as these represented 80% of database. The results of this statistical analysis are shown in Figure 5-2.

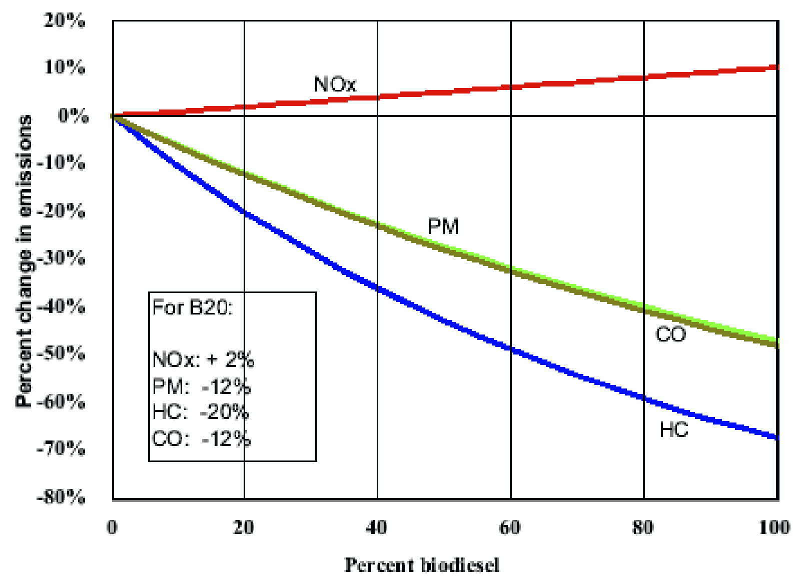


Figure 5-2 Plot of Percent Change in Regulated Emissions with Biodiesel Composition.

In addition to trying to fit all of the available data, the EPA tried to determine from the data, the effects of specific variables, especially:

- Test cycle effects- Their analysis showed that steady-state cycles differed from transient cycles in terms of correlations between emissions of PM and CO and % biodiesel. They excluded all steady-state data from PM and CO analyses.
- Engine standards groups – The EPA database was comprised of predominantly 1989-1997 model year engines, comprising 96% of the data, with 1991-1993 engines comprising 50% of the database. The EPA analysis did show some differences in the 1991-1993 model year group for PM, but no other statistical differences.
- Base fuel effects – The EPA classified fuels into 2 categories: clean and average. The clean fuels would be more representative of California diesel fuel. The EPA analyses showed that for biodiesel blends with clean fuel, the increases in NOx were greater and the decreases in PM were reduced compared to blends with the biodiesel fuel.
- Biodiesel source effects
- Comparison of vehicle data to engine data

The overall trends shown in Figure 1, provide a basis for understanding the effects of biodiesel on emissions. These include reductions in PM, THC, and CO, with a slight increase in NO_x. While this information provides a general guideline on emissions, it is important to put this into the context of Caltrans applications where fuels or operating conditions may differ from the engine dynamometer studies that make of the majority of the EPA database. The effect of biodiesel on each pollutant is reviewed below. An emphasis is made on situations where Caltrans applications might differ from those of the more traditional database.

5.5 NO_x Emissions

The potential impact of biodiesel on NO_x emissions is another critical issue for Caltrans. McCormick et al. (2001) tried to understand the impact of biodiesel chemical structure, specifically fatty acid chain length and number of double bonds, on emissions of oxides of nitrogen (NO_x) and particulate matter (PM). They measured emissions for many very well characterized biodiesel samples and compared them to a #2 certification diesel fuel on an engine test stand. They found excellent correlation between density, cetane number, and iodine number (which is an indicator of the degree of saturation of a molecule), with higher NO_x emissions found for biodiesel blends with higher densities, lower cetane number, and higher iodine number. The fact that the data did not show an apparent PM/NO_x tradeoff suggests that the NO_x increase, relative to petroleum diesel, that is observed for some biodiesel fuel is not driven by the thermal or Zeldovich NO_x formation mechanism but instead by the fuel properties. They concluded, "fuel chemistry is at the root of all of these fuel properties and the increased NO_x emissions observed for many biodiesel fuels."

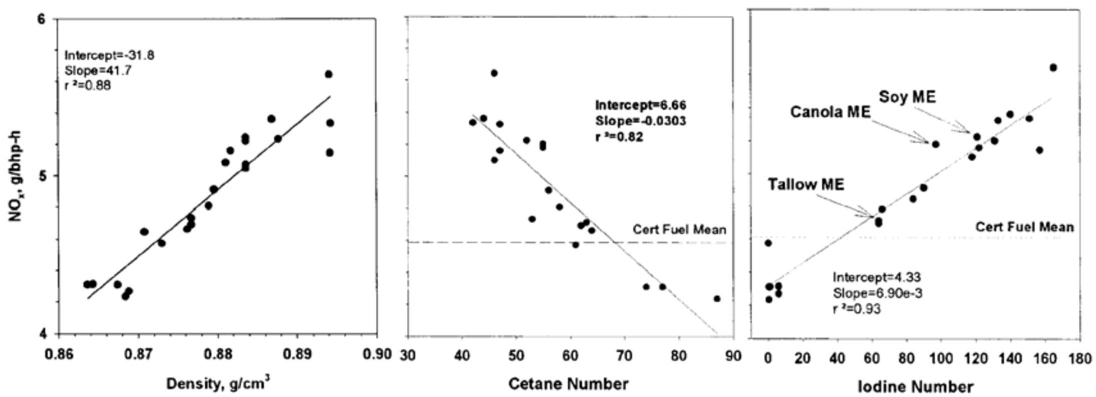


Figure 5-3 Examples from McCormick et al. (2001) Showing Fuels Property Effects on NOx Emissions

Ban-Weiss et al. (2005) from UC Berkeley developed a numerical model to look at increases in NO_x emissions. They postulated that increasing double bonds acted to increase flame temperatures leading to higher NO_x. Double-bonded molecules in particular have higher flame temperatures than single-bonded counterparts. From the numerical models, they concluded that the increased NO_x could be due to the Zeldovich mechanism due to the higher flame temperature of double bonded molecules. This hypothesis is consistent with experimental results showing higher NO_x levels for more highly unsaturated feedstocks (McCormick et al, 2001). In other combustion experiments, Senatore et al. (2000) observed higher flame temperatures for rapeseed biodiesel mixtures compared to those of conventional diesel. School and Sorenson (1993) measured increases in cylinder pressure and maximum rate of pressure increase for biodiesel blends, but did not report to corresponding cylinder temperatures.

As shown in research by McCormick et al (2001) on chemical composition, biodiesels made from different feedstocks can have a different impact on NO_x emissions. It was shown that a B20 produced with YG biodiesel was NO_x neutral; however, with soy, the NO_x was about 2% higher and that cetane improvers could be used to mitigate the NO_x increase. In their more comprehensive analysis, the EPA's (2002) results indicated that emissions depended on the source of the biodiesel feed: soybean oil, rapeseed/canola oil or animal fats. Results from the EPA and other analyses indicate that the biodiesel made from animal fats or yellow-grease has lower NO_x emissions than form either soy or canola oils. Results from the EPA analysis are shown in Figure 5-4 below.

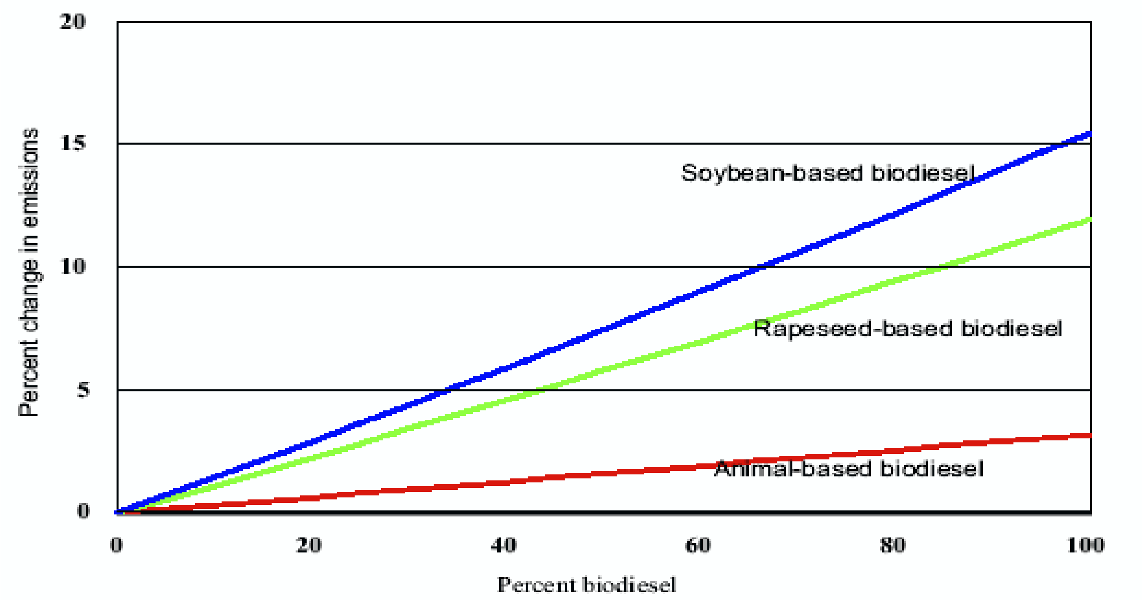


Figure 5-4 Percent Change in NO_x Emissions for Biodiesel from Different Feeds as a Function of Percentage of Biodiesel

An investigative team at Penn State University examined two of the primary causes for NO_x increases during the combustion process in compression ignition (CI) engines and applied that rationale to biodiesel fuel (Szybist et al., 2003). One reason for higher NO_x emissions is that more fuel is consumed during the premixed phase of the combustion process and another reason is an inadvertent advance in the fuel injection timing.

Szybist et al. (2003a) reviewed the premixed and diffusion phases of the combustion process. In the premixed phase, fuel is injected and after a delay, the fuel-rich mixture ignites and quickly reacts all the oxygen. Following the shorter premixed combustion phase, the flame transitions into the much longer diffusion phase where mixing of the fuel and air is the limiting factor. In general, NO_x emissions correlate with the amount of fuel consumed during the premixed phase as the heat released during the premixed combustion phase preheats the reactants for the diffusion phase leading to increased flame temperature and NO_x emissions. The amount of fuel reacted during the premixed phase depends on the amount of time the fuel and air have to mix and the speed of the fuel and air mixing process. The fuel and air mixing process is faster and more efficient for a fuel with a high boiling point range. Szybist et al. also noted that biodiesel has a higher boiling point range than diesel fuel, so more heat should be released during the premixed phase of combustion, leading to higher NO_x emissions.

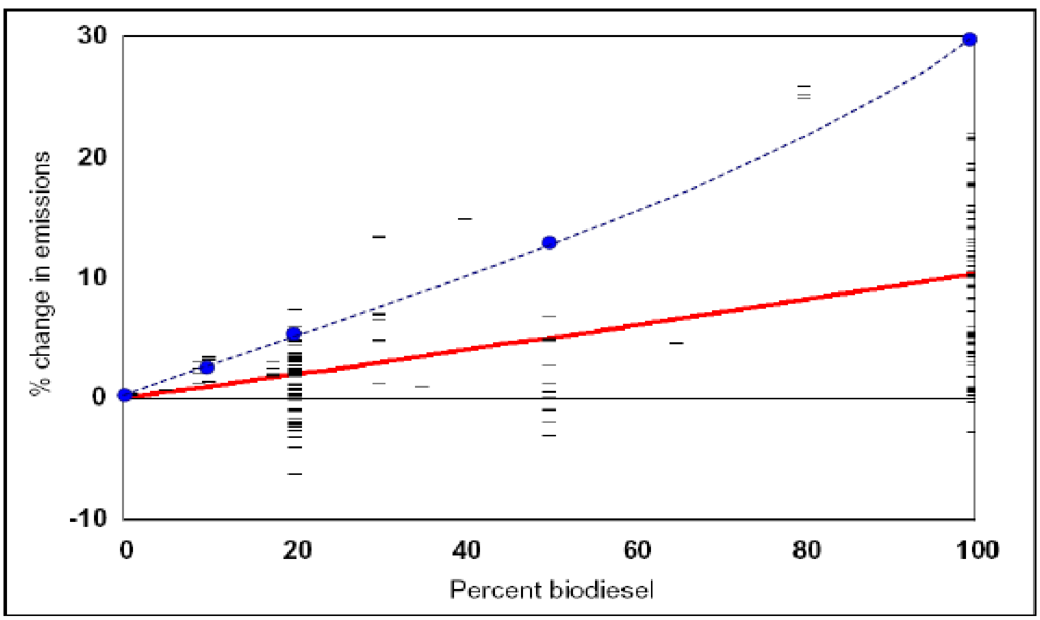
Szybist et al. (2003a) also reviewed the effects of injection timing. Advancing fuel injection timing increases the time before the reaction is quenched by the volume expansion in the cylinder, thus increasing the reaction time and temperature and ultimately increasing NO_x emissions. Several researchers have reported an inadvertent advance in fuel injection timing with biodiesel. Choi et al. (1997) reported an advance in fuel injection timing of 0.6 degrees with B40, and Monyem et al. (2001) reported an advance of 2.3 degrees with B100 and an advance of up to 0.75 degrees with B20.

Van Gerpen and coworkers and Boehman and coworkers have shown that biodiesel causes an advance in the fuel injection timing because of its higher bulk modulus of compressibility [or higher speed of sound] (Van Gerpen, 2000; Szybist et al., 2003b). The higher speed of sound causes the pressure wave from the fuel pump to the hydraulically open the fuel injector earlier, thus advancing the fuel injection timing. Tat and Van Gerpen (2003) calculated the bulk modulus of the individual methyl esters that comprise biodiesel based on speed of sound measurements and showed that for a given carbon number the bulk modulus increases with an increasing degree of unsaturation. Thus, a biodiesel formulation with fewer multi unsaturated methyl esters may reduce the inadvertent advance in fuel injection timing. Van Gerpen (2000) also experimentally showed the impact of bulk modulus on fuel injection timing and NO_x. Szybist et al. (2003a) measured the bulk modulus of a high-oleic acid soy oil to evaluate whether the inadvertent advance in fuel timing could be reduced for a molecule with fewer unsaturated methyl esters. They found that the bulk modulus for the high-oleic acid soy oil was only slightly lower than that of the synthetic standard biodiesel, but it was still significantly higher than that of diesel fuel. In a subsequent study, Szybist et al. (2005) found that by increasing the methyl oleate portion of the biodiesel to 76% the biodiesel NO_x effect could be eliminated and a NO_x neutral blend could be produced, even without a significant change in the injection timing for the biodiesel. For this engine, NO_x emissions were found to be insensitive to ignition delay, maximum cylinder temperature, and maximum rate of heat release. The dominant effect on NO_x emissions was the timing of the combustion process, initiated by the start of the injection, and propagated through the timing of maximum heat release and maximum temperature.

The cetane number (CN) of diesel fuel is used as a quality indicator and is related to the time between fuel injection and ignition. The CN correlates with the amount of fuel consumed during the premixed phase of combustion and thus usually with NO_x emissions. However, biodiesel fuels are more efficient during the fuel and air mixing process, so for a biodiesel blend to have the same amount of fuel reacted during premixed combustion as the baseline diesel fuel, the biodiesel blend requires less time, and thus displays a higher cetane number. Further increasing the cetane number of biodiesel by using additives to improve cetane number has been shown to be effective in reducing NO_x emissions from biodiesel, as discussed below.

Several other hypotheses have been put forth in understanding the biodiesel NO_x effect. It has been suggested that the reduction of PM in the diffusion flame may lead to an increase in flame temperature because of the loss of radiant heat transfer that is provided by PM, being a highly effective heat radiator. Cheng et al. (2006) showed that flame luminosity measurements suggested less radiation from a B100 flame, particularly for light load conditions where NO_x was shown to increase. Another potential NO_x hypothesis could be the enhanced formation of Fenimore or prompt NO, which is formed by the reaction of radical HC species with nitrogen, ultimately leading to formation of NO (Miller and Bowman, 1989). Hess et al. (2005) examined the potential impacts of antioxidants, which have the capability of terminating these kinds of radical reactions. They found that some antioxidants were capable of reducing NO_x emissions for a B20 blend in their engine (butylated hydroxyanisole and butylated hydroxytoluene), while others were not.

While there is a general trend of NO_x increases for biodiesel blends in the EPA data, NREL researchers have recently argued that a more comprehensive examination of the biodiesel emissions and chassis dynamometer testing indicates that B20 does not have a significant impact on NO_x. McCormick et al. (2006a,b) conducted a comprehensive evaluation of the results of engine and chassis dynamometer tests using biodiesel. They included an evaluation of chassis dynamometer studies included in EPA's comprehensive report and studies conducted since the EPA's report. For the more recent chassis dynamometer studies, they found no statistically significant change in NO_x emissions with an average change of 1.2%±2.9% (95% confidence level). EPA's previous evaluation of chassis data showed a trend line of lower NO_x emissions with increasing biodiesel, but this was not statistically significant. These researchers also reviewed engine dynamometer studies that have occurred since the EPA report. They found for the more recent engine dynamometer tests taken as a whole, the average change in NO_x emissions was -0.6%±2.0% (95% confidence level). They also observed in reviewing the data used by EPA that nearly half of the observations were for DDC engines manufactured from 1991-1997 and suggested that could have impacted the representativeness of the data set since DDC engines tend to exhibit a slight increase in NO_x. Finally, these researchers conducted some additional chassis dynamometer tests on eight heavy-duty diesel vehicles, including three transit buses, two school buses, two class 8 trucks, and one motor coach. They found the NO_x emissions impact of B20 varied widely with engine/vehicle technology and test cycle ranging from -5.8% to +6.2%, with an average statistically insignificant change of 0.6%. Combining these results with the other recent chassis dynamometer studies they reviewed, average change in NO_x was 1.2%±2.9% (95% confidence level).



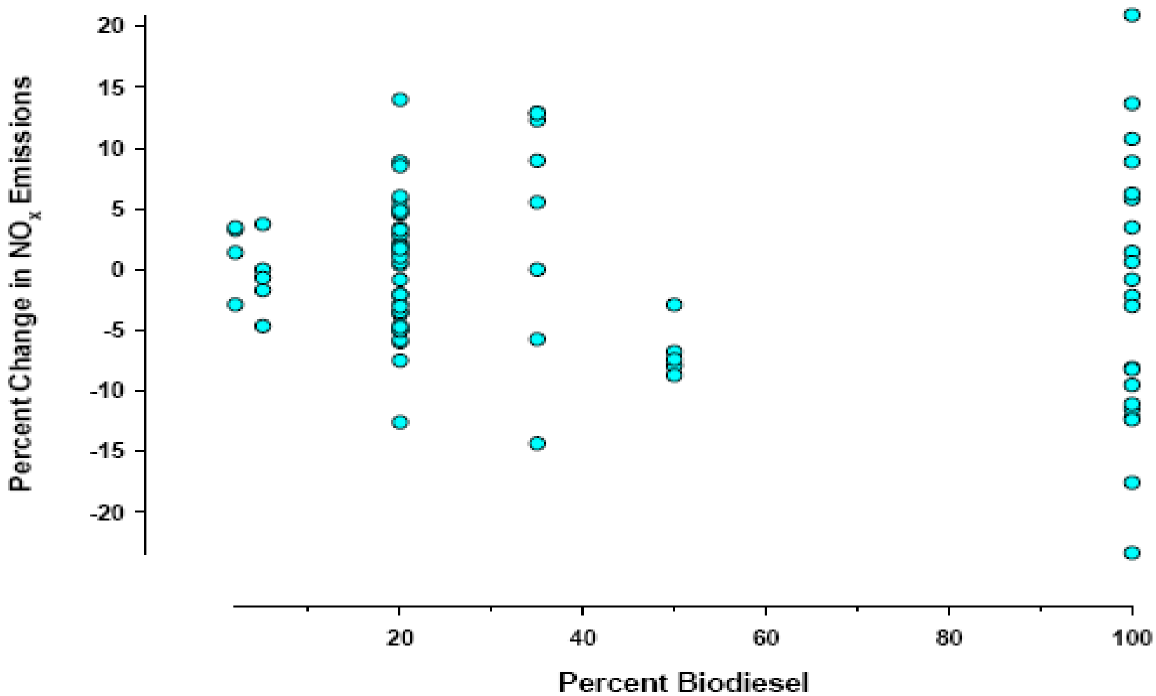


Figure 5-5. Effects of Biodiesel on NOx Emissions for Engine (a) and Chassis (b) Dyno Testing

Holden, Durbin and coworkers conducted a comprehensive study of biodiesel emissions in military vehicles (Holden et al., 2006, Durbin et al., 2007). The study encompassed a wide range of application types including 2 medium-duty trucks, 2 Humvees, a heavy-heavy-duty diesel truck, a bus, 2 stationary backup generators (BUGS), a forklift and an airport tow vehicle. The full range of fuels tested included a California ultra-low sulfur diesel fuel (ULSD), different blend ratios of 2 different yellow-grease biodiesels and 1 soy-based biodiesel, JP-8, and yellow-grease biodiesel blends with 2 different NO_x reduction additives. The fleet average NO_x emissions for a soy-based B20 fuel were not statistically significant and ranged from 0.0% to +1.4 depending on how the results normalized into units of grams of emissions per either gallons of fuel used, kg of fuel used, or BTU's of fuel used.

Other previous chassis dynamometer studies have also not shown any consistent effects for NO_x emissions. Research at UC Riverside also found that NO_x increases were observable for a B100 in chassis dynamometer tests of medium-duty diesels, but not for a B20 blend (Durbin et al 2000a, 2002). Alam et al. (2004) also found that the impact of biodiesel on NO_x was dependent on the engine loading for an AVL 8-Mode test protocol. They found that a majority of the modes showed increases in NO_x for biodiesel, with the exception of the modes 7 and 8, which are higher speed higher load modes that are more heavily weighted. Based on the high weighting of these two modes, it was found that overall NO_x emissions decreased for a B20 blend over the 8-mode cycle. McDonald et al. (1995) also found a decrease in NO_x emissions with a neat soy methyl ester (SME) biodiesel, which was attributed to a shorter ignition delay for the SME compared to the base diesel.

Sharp et al. (2000a) also found that the response of different engines differed with respect to NO_x emission. Their results showed that a Cummins B5.9 engine with a pump line nozzle method and a significantly lower fuel injection pressure showed less sensitivity towards NO_x emissions than a Cummins N14 and DDC Series 50 engines that have electronic injection systems with higher injection pressures. Analysis of engine dynamometer data by McCormick et al (2006) indicate that the increase in NO_x emissions for engine testing may be greater for newer engines compared to older engines.

The use of additives and cetane improvers has been suggested as one method to mitigate increases in NO_x emissions with biodiesel blends. McCormick et al. (2003) examined a number of approaches for NO_x reduction from biodiesel in a study titled *NO_x Solutions for Biodiesel*. The cetane enhancers, di-tert-butyl peroxide (DTBP) and ethyl-hexyl nitrate (EHN), were both effective in reducing NO_x from biodiesel. Treatment with 1% DTBP lowered NO_x by about the same amount for blends from either soy-based or yellow grease biodiesel. They added that if the performance of this engine is representative of the diesel fleet as a whole, a nearly NO_x neutral biodiesel blend can be achieved. Sharp et al (1994) also found that NO_x emissions in a B20 blend could be reduced by using a DTBP additive. In a more recent study, McCormick et al (2005) showed that the use of cetane improvers in newer engines meeting the 2.5 g/bhp-hr NO_x + HC standard did not provide any improvement in NO_x emissions for biodiesel blends. These engines have a much more highly retarded injection timing and are less sensitive to the effect of cetane number. Clark et al. (1984) also found in an earlier study that EHN did not impact NO_x emissions for biodiesel blends.

It has been suggested that timing changes could be used to overcome the observed increases in NO_x with biodiesel blends. In reviewing 1997 and older studies of two stroke engines, Graboski and McCormick (1998) found that for various two stroke engines, NO_x emissions decreased from 1.9 to 7.3% per degree of timing retard with a 4 maximum change investigated. Simultaneously, PM emissions increased by 0.5 to 8.5% relative to B20 with no timing change. Graboski and McCormick found similar trends for earlier four stroke engines. They also noted that for a given engine, the effects of timing change on NO_x and PM were observed independent of fuel type, such that at a given degree of timing retard, the baseline was typically still lower in NO_x than the a biodiesel blend at the same timing. Starr (1997) showed that NO_x emissions decreased by 14% and 21%, respectively, when the timing was retarded by 3 and 5 degrees, with slight increases in PM emissions. Scholl and Sorenson (1993) also found large reductions in NO_x emissions for biodiesel blends when retarding the timing 5 degrees. In comparing results at different timings and cylinder pressures, they found that the difference in NO_x emissions for the different fuels could be attributed directly to changes in ignition delay and burning rate. It should be noted that while timing changes for a specific engine may be used to reduce to reduce NO_x emissions on biodiesel blends, timing changes would also provide corresponding reductions in NO_x emissions for a straight diesel fuel, such that some impact of biodiesel could still be observed under similar conditions.

Advanced combustion strategies may also help to mitigate any NO_x related issues for biodiesel. Researchers at Oak Ridge National Laboratory have been studying homogeneous charge compression ignition engines (HCCI) and high efficiency clean combustion (HECC) engines (Szybist, et al. 2006). HCCI engines utilize compression autoignition like a diesel engine, but the fuel air mixed is premixed like a spark ignition engine. The HCCI strategy can provide emissions benefits in NO_x by reducing local maximum temperatures and in PM by reducing fuel rich regions that occur during standard diesel combustion. For an HCCI engine, they found that biodiesel blends showed similar NO_x and energy efficiency compared to a base diesel fuel, for blends up to 20%. For the HECC engine, emissions for a B5 fuel showed no change in NO_x, although the B5 blends did show different effects in HC and formaldehyde depending on the base.

5.6 PM Emissions

PM emissions generally show a decreasing trend with increased biodiesel use. The formation of PM predominantly occurs in locally fuel rich zones during the diesel combustion process. The oxygen content of biodiesel is considered the main factor in soot reduction of biodiesel, which can act to reduce these fuel rich zones. Sharp et al. (2000a) found a nonlinear trend in the reduction in PM as a function of oxygen content. In this study PM reductions, increased in going from a 2 to 11% oxygen content with the response dampening at higher oxygenate levels. Graboski and McCormick (1996) also found a reduction in PM with increasing oxygen content for a larger range of studies. McCormick et al (1997) found PM reductions for fuels with different oxygenates, ranging from 10 to 15% reductions with fuels with oxygen contents of 1 to 2%. Other researchers such as Liotta and Montalvo (1993), Tsurutani et al. (1993) have also PM reductions as a function of oxygen content for a range of oxygenate compounds. Researchers at the JOMO Technical Research Center have suggested that both the addition of oxygen and the reduction in aromatics could contribute to the overall reduction in PM emissions observed for biodiesel blends (Uchida and Akasaka, 1999; Akasaka et al., 1997)

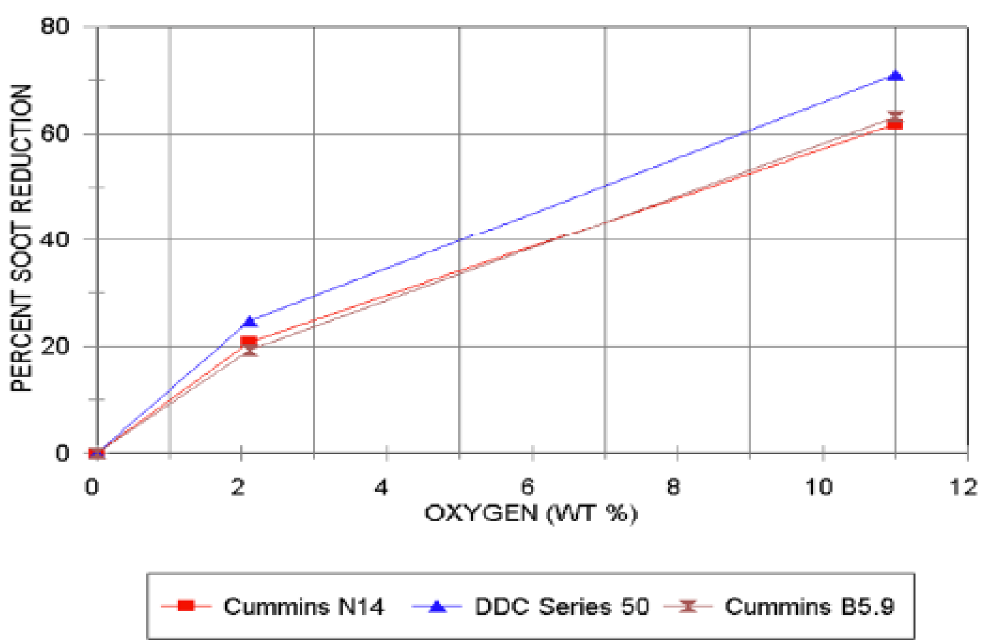


Figure 5-6. Fuel Oxygen Content vs. Engine Out Soot

To understand the nature of the PM reductions, it is useful to look at the composition of the PM. PM from diesel sources is considered to be predominantly composed of elemental soot and a soluble organic fraction. The elemental soot is generally a product of the combustion process in the fuel rich zones. The soluble organic fraction can be comprised of unburned fuel or lubricating oil. Sharp et al. (2000a) examined the composition of the PM and found that the PM reductions from biodiesel were predominantly in the elemental soot portion of the PM.

Some studies have shown increases in the volatile organic fraction of the PM with biodiesel. Because of the low volatility, the unburned esters will condense on the filter and be measured as SOF. In some cases, under lower load operating conditions the increase in volatile organic fraction can be greater than the decline in nonvolatile PM, leading to an increase in total PM. Several researchers have shown that at low loads, PM emissions can increase due to an increase in the soluable organic fraction of the PM (Choi et al. 1997, Akasaka et al. 1997, McDonald et al. 1995, Last et al. 1995, and Chang and Van Gerpen [1998]). Cheng et al. (2003) also found increases in PM at a medium engine load for a B100 due to increases in SOF. The characteristics of the SOF for biodiesels was modeled and examined under different experimental conditions by Chang and Van Gerpen (1998). Graboski and McCormick (1996) also found that the PM reductions achieved from biodiesel decreased as the SOF portion of the PM increased for a particular engine.

In some more recent work, Song et al. (2006) studied the oxidation behavior of biodiesel soot using a combination of techniques such as transmission electron microscopy (TEM), electron energy loss spectra (EELS), and Fourier Transform Infrared (FTIR) to examine the microstructure of soot. These researchers found that B100 soot is far more reactive than other diesel soots and has a significantly different oxidation process. The B100 oxidation process is unique in that the soot undergoes a structural change in the outer band and subsequent hollowing out at an early stage. This process emphasizes the importance of the initial oxygen surface groups as opposed to the initial structure and pore size distribution. The incorporation of greater surface oxidation functionality in the B100 soot provides the means for rapid oxidation and drastic structural transformation during the oxidation process.

Chassis dynamometer results have shown some different trends under different experimental conditions and with different types of vehicles. Graboski and McCormick (1996) reviewed early chassis dynamometer studies and found that emissions of PM were found to decrease for biodiesel blends for engines that did not have a high percentage of PM as oil, but did not show consistent trends for high oil use engines. This could be due in part to increased testing variability. Graboski and McCormick (1996) and The Adept Group (Spataru and Romig, 1995) showed reduction of 46.8% and 6.1%, respectively, for chassis dynamometer tests conducted on buses with 6V92TA engines. McCormick et al. (2006) showed reductions of ~18% for two in-uses with 2000 Cummins ISM engines. Peterson and Reece (1996) observed increases in PM emissions for two Dodge pickup trucks, although the biodiesel had substantial amounts of glyceride inpurities. Durbin et al. (2000a, 2002) tested a wider range of diesel pickup trucks and found little change in PM emissions for a biodiesel blend using a California diesel as the baseline fuel. In a more recent study, Holden, Durbin and coworkers did not find statistically significant PM changes for B20 for a fleet of military vehicles/equipment. In some cases, PM reductions were observed at higher blend levels, however. Schramm et al. (1999) found PM emissions increased with biodiesel over chassis dynamometer test cycles designed to be representative of driving in Copenhagen, Denmark. For the light-duty chassis FTP, the operation load on the engine can be quite different from an engine test, since the light-duty FTP has relatively limited operation near full load conditions for the vehicle or engine.

PM reductions can also be a function of different engine types. Graboski and McCormick (1996) examined earlier emissions test data from four stroke DDC series 60 and Cummins L-10, N-14, and B5.9 engines. They observed that the emissions reductions in PM appeared to be greater for the DDC engines in comparing to the Cummins engines. The differences could be related to differences in the approaches used by the different engine manufacturers to optimize the NO_x/PM tradeoff. McCormick et al. (2005) observed that PM reductions for two new engines were on average more than twice as large as those characterized by EPA for older engines. Graboski and McCormick (1998) found in their earlier literature review that PM reductions become more significant in engines with a lower SOF fraction. Lower SOF is characteristic of newer engines with low miles or hours of operation. In older worn engines, the impacts of oil consumption can be greater, reducing the impact of the biodiesel on PM.

McCormick et al (2001) also investigated the importance of feedstock on biodiesel PM reductions. Their results showed that PM reductions for different biodiesels were similar as long as the fuel density was less than 0.89 g/cm3 or the cetane number was greater than 45.

The PM size and particle number are also important factors in evaluating the health effects of PM emissions. Schroder et al. (1999) compared the size distributions of a rapeseed-based B20 with those of a base diesel fuel and found higher numbers of particles for the B20 fuel over a 13-mode cycle. This was consistent with higher mass fractions observed for the B20 at nearly all size cuts measured with an impactor. The increase in mass was attributed to an increase in SOF.

Another more indirect measure of PM that is often used in field testing situations is opacity. Opacity is generally measured by a smoke meter using a snap an idle test where the engine is accelerated to the maximum governed engine RPM and returned to idle several times. UCR researchers have conducted several studies of the effects of biodiesel on opacity. This includes studies of construction equipment at a local landfill (Durbin et al., 2000b), municipal fleet vehicles such as garbage trucks (Durbin et al., 2000), and buses operating at Yosemite National Park. Of the 10 vehicles tested for these studies, a majority showed opacity reductions with the biodiesel fuels (Durbin et al. 2005b), with reductions on the order of 5-30% for a range of different biodiesel blend levels. There was also a general trend of greater opacity reductions for higher blends of biodiesel. Fosseen Manufacturing and Development (1995a) reported reductions in opacity of approximately 20% for tests on a bus fleet in an earlier study.

Lucas published a report of the demonstration on various U.S. Army tactical wheeled vehicles from March 1994 through March 1995 at the U.S. Army Yuma Proving Ground (YPG). Testing was conducted to compare vehicle system performance when the vehicles were operated with 80/20 percent JP-8/Bio-diesel fuel blend instead of neat (or 100%) JP-8 fuel. The snap idle/smoke opacity measurements before and after fuel change indicted a reduction in the opacity reading after the bio-diesel blend was introduced. Three of the vehicles had an initial snap idle opacity reading of 25-percent or greater, when operated with DF-2. The opacity readings for these vehicles were reduced by 19-, 28-, and 48- percent, after bio-diesel blend was added. These three vehicles also showed a tendency for the opacity measurements to continue to decrease with continued use.

Ortech Corp. (1995) also found reductions in smoke for B10 and B20 biodiesel blends for a four-stroke engine test, as opposed to a snap and idle test. They found the greatest reductions under lugging conditions where the B10 reduced smoke by 29% and the B20 reduced smoke by 50%. In another study, Fosseen Manufacturing and Development (1995b) found no significant changes in smoke opacity for a two-stroke engine tested on biodiesel.

For opacity, it is important to note that light extinction in diesel exhaust is primarily attributable to the elemental carbon portion of the particulate (Japar et al., 1984; Moosmuller et al., 2000). As discussed above, several studies have shown biodiesel fuels can have higher fractions of organic carbon relative to elemental carbon in the PM than those for standard diesel. This change in chemical composition could cause a reduction in the observed opacity even in the absence of reductions in total PM. As such, opacity can not be considered a true measure of PM emissions benefits.

5.7 CO Emissions

CO emissions are less of a concern for diesel engines due to their typically lean operation. CO emissions are formed as a result of incomplete combustion. CO emissions tend to decline with the addition of increasing levels of biodiesel, which can be attributed to the impacts of oxygen in the fuel on combustion in localized areas. Several researchers have observed a good correlation between CO emissions and PM emissions (Wang et al., 2000; Choi et al., 1997; EPA, 2002). The vast majority of studies have shown reductions in CO emissions with biodiesel, although there are some exceptions under different test conditions (Akasaka et al., 1997; Ziejewski and Goettler, 1992; Choi et al., 1997). McCormick et al (2005) that CO emissions for biodiesel blends were reduced for newer engines, but that the percentage reduction was less than for older engines. Durbin et al also found little change in CO emissions for chassis dynamometer tests of medium-duty diesel vehicles using a California diesel as the base fuel.

5.8 THC Emissions

THC emissions result from unburned fuel and are generally lower for diesel compared to gasoline combustion. HC emissions can form in areas of combustion that are either too lean or too rich to autoignite, and in volumes or crevices of the combustion cylinder where these conditions can occur. The addition of biodiesel generally reduces emissions of THC, as observed in the vast majority of engine tests and the trends found by EPA in their statistical analysis. In a limited number of test programs McCormick et al. (2005) did find that there was not statistically significant decrease in THC emissions for two newer engines. Durbin et al. (2000a, 2002, 2007) saw reductions in THC for most, but not all, vehicles with various biodiesel blends for testing conducted on a light-duty chassis dynamometer cycle. Schramm et al. (1999) observed that a base diesel fuel had lower emissions compared to a commercial biodiesel blend.

Potential sampling artifacts for HC emissions with biodiesel fuels have been investigated by some researchers. Since the gaseous HC emissions of biodiesel tend to have a lower volatility compared to diesel fuel, it has been suggested that some condensation might be occurring in the sampling lines, even at 190°C, that could lead to lower THC emissions for biodiesel. Chang and Van Gerpen (1998) showed that there is some increase in THC emissions as the sampling heated line is increased above 190°C for both diesel #2 and biodiesel, but they concluded that condensation was not responsible for the reductions in THC typically observed for biodiesel. McDonald et al. (1995) also noted the possibility of condensation in the sampling line for THC, but their measurements of the FID response to exhaust stream injection of SME indicated that this effect was small compared to the concentrations measured.

5.9 Greenhouse Gas and CO_2 Emissions

The use of renewable biodiesel in place of petroleum diesel also provides important advantages for greenhouse gas emissions. Because biodiesel is produced from renewable sources which can function as part of the natural CO_2 cycle, the increase in CO_2 emissions is small compared to the direct use of fossil fuels. Overall, there is slightly less than a one to one benefit in greenhouse gas reduction with biodiesel. For B100, the reduction in net CO_2 emissions is 78.45% compared to petroleum diesel (USDA and DOE, 1998). The reduction in net CO_2 emissions for B20 is 15.66% compared to petroleum diesel. The lifecycle CO_2 emissions for the biodiesel are the result of operating equipment in the processing and farming related to the biodiesel and in transportation of the fuel.

5.10 Unregulated Emissions and Toxicity

Section 211(b) of the Clean Air Act Amendments specifies that new motor vehicle fuels or fuel additives for commercial use will not present an increased health risk to the public (Code of Federal Regulations [CFR] Title 40, Part 79, Section 70.55). To ensure meeting that goal, EPA established a fuel and fuel additive registration program including a set of testing protocols that are designed to provide sufficient data to assess the impact of a given fuel or additive on the potential health risks posed by motor vehicle exhaust. The Tier 1 requirements of these test protocols include a detailed characterization of the exhaust emissions of one or more engines while operating with the fuel or additive in question (CFR Title 40, Part 79, Subpart F, Section 70.52). Since biodiesel was proceeding as a commercial fuel, the National Biodiesel Board (NBB) initiated a literature review and test program at Southwest Research Institute (SwRI) involving a detailed characterization of both regulated and unregulated exhaust emissions from current technology to satisfy the Tier 1 requirements.

Results from the literature review indicated that considerable data were available on the effect of biodiesel on regulated pollutants (HC, CO, NO_x, particulate matter) but most of this data was generated using older technology engines. Further, very little detailed exhaust characterization data on biodiesel beyond the regulated pollutants existed. In order to address these needs, transient exhaust emissions from three modern diesel engines were measured both with and without an oxidation catalyst. Emissions were characterized with neat biodiesel and with a blend of biodiesel and conventional diesel fuel. Regulated emissions, performance data and detailed chemical characterization of exhaust emissions were presented in a series of papers (Sharp et al., 2000a,b).

SwRI's results showed that the use of biodiesel resulted in lower emissions of unburned hydrocarbons, CO, and PM, with some increase in emissions of NO_x on some engines. Biodiesel also appeared to enhance the ability of the catalytic converters to reduce particulate emissions. With its high oxygen content, neat biodiesel fuel generally resulted in a measurable loss of engine power and an increase in fuel consumption. Chemical characterization revealed lower levels of some toxic and reactive hydrocarbon species when biodiesel fuels were used. In addition, emissions of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAH compounds were substantially lower with biodiesel, as compared to conventional diesel fuel. Analytical results showed that the emissions did not generate any unexpected hydrocarbon species.

Durbin et al. examined the more detailed species for medium-duty vehicles fueled on biodiesel blends and different CARB fuels. In one study, a low aromatic-high cetane fuel generally performed well in comparisons with the other base fuels and the biodiesel blends (Durbin et al. 2001). Some biodiesel blends were found to have a higher element and ion contribution to the PM, although elemental and organic fractions for this study did not show significant fuel differences. For 3 of the 5 vehicles, the low aromatic-high cetane diesel fuel had the lowest PAH emissions. The biodiesel blends generally had PAH emissions comparable to or lower than the CARB fuel. In the other study, one vehicle showed a significant reduction in overall aromatics with B100 while the HC speciation profiles for the other vehicle were similar between fuels, with the exception of lower benzene levels for the B100 (Durbin et al. 1999). In another study of chassis tests on a diesel van, Schramm et al. (1999) found reductions in PAHs for RME biodiesel blends. Smith et al. measured speciated HCs and aldehydes and ketones, but the background levels in this study precluded conclusions regarding fuel effects. The compounds in the SME exhaust were similar to those found in the diesel exhaust, with the exception of the compound methyl acrylate.

The Motor Test Center (MTC) in Sweden conducted several chassis dynamometer test programs where unregulated emissions were measured (Gragg et al. 1994, 1998). Tests on a Scania bus showed approximately a 60% reduction in PAHs compared to a test fuel with properties similar to CARB diesel. On a Volvo bus, the combined semi-volatile+PM PAHs emissions were comparable to those of a diesel fuel with similar properties to a Fischer-Tropsch diesel fuel (~95% paraffins).

Bouche et al. (2000) conducted tests on an off-road engine at different load points. They found that aldehyde emissions were mixed with respect to biodiesel with some modes showing decreases and some modes showing increases with biodiesel use.

Havey et al. (2005) conducted some preliminary testing on nitro-PAHs in biodiesel and diesel exhaust samples from a 2002 Cummins ISB 300 engine. This engine was designed to meet 2004 EPA emissions requirements and was equipped with a cooled-EGR, high pressure common rail injection, and a variable geometry turbocharger. Overall, the diesel sample showed a wider range of nitro-PAH compounds, but further qualitative and quantitative comparisons are in process.

5.11 Biodiesel Emissions Impacts as a Function of Engine Operating Condition and Comparisons Between Chassis vs. Engine Dyno Results

A survey of the literature indicates some differences may exist between chassis and engine dynamometer testing. Recently, researchers at NREL have observed decreases in NO_x emissions for chassis dynamometer tests conducted on two in-use buses, in contrast to the increases more typically seen for engine dynamometer tests. As discussed above, McCormick et al also found no significant increases in biodiesel blends for a broader survey of the literature on chassis dynamometer tests. Wang et al. found differences in the effects of a B35 blend on NO_x emissions for different engine types. They found that NO_x emissions increased for the late 1980s Cummins engines from 3-6%, but for the early 1990 model Detroit Diesel engines, NO_x emissions were found to decrease from 2-7% when using the B35. Tests at the MTC in Sweden for two buses showed relatively strong increases in NO_x emissions, however, ranging from ~9% at a B30 blend up to 18 to 30% for B100 (Gragg et al. 1994, 1998).

Some studies of light- and medium-duty vehicles have also shown smaller reductions or even increases in PM for biodiesel blends relative to baseline fuels. Durbin et al. (2000a, 2002) showed over a range of medium-duty diesel trucks that PM emissions of biodiesel were comparable to those of a typical CARB base fuel. Peterson and Reece (1996), Taberski and Peterson (1998) found increases in PM for tests conducted on medium-duty trucks at the Los Angeles MTA Test facility. Schramm et al. (1996) did not find consistent trends in PM emissions for biodiesel for a diesel van, although changes in PM could be attributed to differences in the SOF fraction of the PM. Krahl et al. (1996) also found differences with test cycle for biodiesel blends with rape methylester. Studies for the light-duty FTP showed reductions on the order of 0-20%, while studies over a 13-mode showed reductions from 0-60% depending on the engine type, with some 13-mode tests on a direct injection engine also showing increases from 20 to >100%. Tests conducted at the MTC in Sweden did, however, show relatively strong ~40% reductions in PM for an RME compared to a petroleum diesel for a VW Golf over the new European Driving Cycle (NEDC) (de Serves, 1999). Siram et al. (2000) also found reductions in PM of about 19% for a steady state 13 mode cycle for a 125 hp DI Mercedes Benz diesel engine. Graboski and McCormick (1998) also noted that for steady state emissions tests, PM was highly dependent on the engine or chassis cycle used, with PM increasing and NO_x going down under some conditions. There was sufficient variability in the steady state data, however, to preclude general conclusions on the different response of biodiesel under different conditions.

More recently, researchers at the US EPA and Cummins Inc. have studied the impacts of engine operation/load on biodiesel emissions more directly. The US EPA evaluated the impact of engine load on biodiesel emissions over a series of different test cycles (Cze et al. 2007). These test cycles included an FTP, a UDDS, a high speed cruise cycle, a second high power cycle based on the high speed cruise cycle, a nonroad engine certification cycle, and a potential world-wide certification cycle. Testing was conducted on a 2006 Cummins ISB engine using a paired series of fuel tests with B5 to B50 soy-based biodiesel blends. Average NO_x emissions were found to increase over each cycle, ranging from 0.9% to 6.6% and from 2.2 to 17.2% for the B20/B0 and B50/B0 fuel pair, respectively. Except for the most lightly loaded cycle, the NO_x increases were statistically significant for all biodiesel fuel pairs. Significant reductions in CO and PM were also observed over a majority of the cycles tested. Generally, the trend of higher NO_x and lower PM emissions for biodiesel were found to increase with increasing average cycle power. This trend was also found for additional chassis dynamometer data that was included in some supplementary analysis. The results of this study indicate that irrespective of cycle type or testing method (i.e., engine or chassis dynamometer), the biodiesel impact appears to be directly related to the fuel consumption or the average cycle power (load) in this type of engine.

Researchers at Cummins Inc. conducted a series of controlled tests on a single cylinder engine (Eckerle et al. 2008). These data were then used to calibrate a KIVA chemical kinetics model to determine how the biodiesel blend affects NO_x production during the combustion process. The combustion effect was separated into two factors: flame temperature effects and ignition delay effects. The effects of engine controls specific to the engine calibration were also examined. At higher loads, changes in engine control settings due to the lower energy content of the blended biodiesel were found to be the most significant factor in increasing biodiesel NO_x emissions. The fundamental combustion effects, characterized by diffusion flame combustion, represented a smaller impact on biodiesel emissions. Taking into account both the combustion and engine control effects, the net NO_x effect of B20 at high loads is an increase of 4-5% At lighter loads, pre-mixing and ignition delay play a more important role in NO_x emissions. B20 blends had a higher cetane and shorter ignition delay which contributed to higher NO_x emissions at light loads. At low loads, the net NO_x effect was less than 1% for a low cetane B20 and was a net decrease of 5% for a high cetane B20.

5.12 Comparisons with California Fuels

In a majority of the studies available in the open literature, biodiesel blends are typically compared with base fuels that do not meet the specifications of CARB diesel fuel that is sold in the State. These base fuels typically have higher aromatic contents and lower cetanes numbers than CARB fuels. The EPA made some comparisons of different base fuels and found that the benefits of biodiesel for PM reduction was reduced compared to CARB diesel and that the increases in NO_x emissions were greater for biodiesel fuels when compared with CARB diesel (US EPA, 2002). Clark et al. (1999) conducted tests at West Virginia University on a Navistar T444E engine. These tests included a CARB diesel fuel and different biodiesel blends, although the biodiesel was blended with a low-sulfur off-road diesel fuel. Even when comparing the CARB diesel to biodiesel blended with a lower quality diesel fuel, PM reductions for the biodiesel blend were still observed for this study. NO_x emissions were higher for the biodiesel blends, but much of this increase could be attributed to the increase in NO_x from the off-road diesel base fuel. Similar results were also observed by Starr et al. for biodiesel blends with an EPA base fuel compared to a CARB diesel over a set of 3 different engine timings.

Spataru and Romig of The ADEPT Group conducted chassis and engine dynamometer comparisons between biodiesel blends with CARB base fuels. Chassis dynamometer tests over the Central Business District (CBD) cycle showed that the B20 SME blend decreased THC, CO, and PM emissions by 16.7%, 20.2%, and 6.1%, respectively, while increasing NO_x by 4.5% compared to the CARB baseline diesel. Similar trends were observed in the engine testing with decreased in PM, THC and CO with an increase in NO_x. The decrease in PM emissions could be attributed to reductions in the insoluble PM, while some increase in the soluble PM was found.

The CARB fuel for this testing had a lower cetane number and lower API gravity than typical current in-use CARB fuel. The aromatics content was not given.

Durbin et al. (2000a, 2002) made comparisons of biodiesel fuel with a CARB diesel fuel for a series of medium-duty diesel trucks over the light-duty FTP. The results for these tests were mixed with PM emissions for the biodiesel blends more comparable to those for the CARB diesel. These findings could be related to the differences in the base fuel or to differences in the operational loads that are found over the lower load, light-duty FTP.

5.13 California Biodiesel Study for Low Carbon Fuel Standard

The State of California is emphasizing and implementing legislative requirements that promote the increased use of alternative fuels in California to reduce oil dependency, air pollution, and greenhouse gas emissions. California Governor's Executive Order S-1-07, Low Carbon Fuel Standard (LCFS), requires at least 10 percent reduction of the carbon intensity of California's transportation fuels by 2020. The California Air Resources Board (CARB) is currently conducting a comprehensive study of biodiesel to better understand the impacts on NO_x emissions from diesel vehicles, as well as toxic emissions (Durbin et al. 2008). This program is incorporating engine testing, chassis dynamometer testing, and testing of non-road engines on a range of biodiesel and renewable diesel fuels. A total of at least 7 different engine/vehicle combinations will be tested. This will include heavy-duty diesel engines from different vintages, including a 2007 engine, a 2004-2006 engine, a retrofitted engine, and two non-road engines. The testing will also include at least two biodiesel feedstocks tested on blend levels of B5, B20, B50, and B100, one or more renewable diesel fuels and various blends of these fuels, and other fuel formulations/additive combinations designed to mitigate any potential increases in NO_x emissions. Testing will also be conducted on several cycles designed to represent low, medium, and high power engine operation such that the effects of biodiesel on NO_x emissions can be understood over a range of different operating conditions. The results from the first sets of vehicles and engines will be presented.

5.14 Non-Road Applications

Studies for non-road engines are more limited in the literature. Non-road engines are typically tested over a series of loaded mode steady-state tests. Graboski and McCormick (1998) reviewed some early studies of off-road applications. Goyal tested a Deere 4045T engine over an ISO 8178 8-mode steady state tests. The biodiesel emissions showed a 10% NO_x increase and a 4% PM decrease, with a 4-6% power loss. When the fuel pump was adjusted for equal engine power, NO_x emissions were found to decrease slightly with a 12% increase in PM. Schumacher et al. tested 5 tractors over the ISO 8-mode steady state test and found that smoke was reduced with most soy diesel blends, with reduction of 50-70% for the neat soy biodiesel.

McDonald et al. (1995) conducted tests on a Caterpillar 3304 that is representative of engines used in underground mine applications. They examined emissions over an ISO 8-mode cycle and over two in-house transient cycles of 160 seconds designed to represent light-duty and heavy-duty loads. The results showed reductions in PM for both the transient and steady state tests with the neat SME, although a decrease for a 30% SME was not statistically significant. When a DOC was combined with the biodiesel blends further reductions were obtained, as discussed below.

Bouche et al. (2000) compared the emissions, performance and durability of two different tractor engines with a RME biodiesel. Emissions were measured using a ISO 8178-4 cycle for off-road engines. They found typical trends of decreasing PM, THC,and CO, with increasing NOx. These trends were associated with an increase in the mass fraction burned and the mean cylinder temperature for the RME blend, as well as the addition of oxygen. They also demonstrated the effectiveness of diesel oxidation catalysts (DOCs) with the tractors, as discussed below.

5.15 Biodiesel Use with Aftertreatment Devices

The introduction of Federal and California regulations has or will be pushing the implementation of aftertreatment devices in the diesel marketplace, either for new engines or retrofits. Although the exhaust stream of biodiesel emissions is in a general sense similar to that of the straight diesel emissions, there are some differences that could impact aftertreatment performance. PM emissions for biodiesel blends tend to be lower, which could reduce the amount of regeneration required for the system. This PM also tends to have a higher organic fraction, which could be more readily catalyzed. The burning of soot with nitrogen dioxide is generally a key component for the operation DPFs. Since there is a small increase in NO_x emissions (mainly NO), this could have some impact on the DPF performance. Another aspect of biodiesel is that it has no sulfur and hence it is compatible with the low sulfur fuel requirements that aftertreatment systems have.

Williams et al. (2006) have evaluated the impact of biodiesel and biodiesel blends on DPF performance. The results showed that the balance point temperature for the DPF is approximately 45°C lower for a B20 blend than for the base diesel fuel. A similar result was also observed by researchers from Pennsylvania State University (Boehman et al., 2005). The balance point temperature is the inlet temperature at which the rate of particle oxidation approximately equals the rate of particle collection. The filter regeneration rate was also found to increase significantly, as assessed by monitoring the DPF backpressure as a function of time after pre-loading with particles and ramping to high exhaust temperature. These are both positive traits for biodiesel and might allow passive DPFs to be used in lower temperature engine duty cycles. The use of biodiesel also lowered the total PM output from the DPF by 67% compared to the base diesel, although given the low output of the DPF, these differences would be relatively small on an absolute scale. The use of B20 also caused a 2.9% increase in fuel consumption compared to the diesel fuel. The DPF itself caused approximately a 2% fuel economy penalty irrespective of the fuel used.

The performance of biodiesel with oxidation catalysts has also been shown to be beneficial. Sharp et al. (2000a) showed that the catalyst efficiency for an oxidation catalyst was generally higher for biodiesel blends for PM and the SOF portion of PM. This can be attributed in part to the complementary action of the biodiesel which reduces the elemental soot in combination with the OC that effectively oxidizes the SOF. The catalyst efficiency with biodiesel blends increased for CO on one engine but not the other, while the HC efficiency declined on the only engine where this was measured. Bouche et al. (2000) also found that the PM levels in the exhaust beyond the aftertreatment device were 37% lower for the biodiesel blends compared to the diesel fuel operation. This is in contrast to the engine out emissions which were actually slightly higher for the biodiesel blend. McDonald et al. (1995) also found that for a B30 blend with a OC, total PM emissions were 35% lower compared to the base diesel fuel and 20% lower compared to the base diesel fuel with an OC.

5.16 Air Quality

NREL took their research in a different direction when they contracted with Environ to produce a series of five studies related to air quality and health. The findings are collected in the final report: *Impact of Biodiesel Fuels on Air Quality and Human Health, Summary Report.* The authors analyzed emissions for several areas and considered three fueling scenarios: (1) a standard diesel base case; (2) a 100% penetration of B20 biodiesel in the heavy-duty diesel vehicle fleet (HDDV) fleet; and (3) a 50% penetration of B20 biodiesel in the HDDV fleet. Table 5-1 summarizes the estimated peak pollution concentrations for the standard diesel and 100% B20 emission scenarios and the maximum increases and decreases that occurred anywhere in the region between the 100% B20 and standard diesel fuel scenarios. The increases or decreases in modeled ozone, CO, $PM_{2.5}$, and PM_{10} ambient concentrations due to the widespread use of biodiesel are extremely small (<± 1%) for all air pollutants, locations, and averaging times studied. Total conversion to biodiesel (100% B20) is estimated to reduce risk to exposure to air toxics in the South Coast Air Basin associated with air toxics by approximately 5%. The authors added an important caveat to their summary: "The changes in air pollutant concentrations are below the resolution of the measurements that are typically reported to the State and EPA compliance databases, so that the impacts of biodiesel would not be measurable."

Location	Pollutant	Avg. Time	Units	Federal Standard	Peak Predicted Concentration			Maximum Change	
					Diesel	100% B20	Diff	Increase	Decrease
Northeast Corridor	Ozone	1-Hour	ppb	124	177	177	<1	+0.20	-0.25
Lake Michigan	Ozone	1-Hour	ppb	124	178	178	<1	+0.09	-0.53
Southern California	Ozone	1-Hour	ppb	124	176	176	<1	+0.25	-1.20
Northeast Corridor	Ozone	8-Hour	ppb	84	155	155	<1	+0.15	-0.20
Lake Michigan	Ozone	8-Hour	ppb	84	158	158	<1	+0.09	-0.40
Southern California	Ozone	8-Hour	ppb	84	145	144	<1	+0.15	-0.96
Las Vegas	CO	1-Hour	ppm	35	18.4	18.4	<1	0.00	-0.03
Las Vegas	CO	8-Hour	ppm	9	13.7	13.7	<1	0.00	-0.02
Southern California	PM_{10}	Annual	$\mu g/m^3$	50	75.8	75.6	<1	+0.04	-0.31
Southern California	PM_{10}	24-Hour	$\mu g/m^3$	150	187	186	<1	+0.62	-1.61
Southern California	$PM_{2.5}$	Annual	$\mu g/m^3$	15	52.7	52.4	<1	+0.04	-0.30
Southern California	$PM_{2.5}$	24-Hour	$\mu g/m^3$	65	178	178	<1	+0.62	-1.61
Southern California	Risk	Annual	1:Million	NA	1,257	1,191	-66	NA	NA

Table 5-1 Change in Estimated Pollutant Concentration and the One-in-a-- million Risk Due to Exposure to Air Toxics with the whole HDDV Fleet Using B20 for a Number of Locations.

5.17 Health Effects Studies

Studies have also been investigated to evaluate the health effects of biodiesel through either animal studies or mutagenicity of extracts or other studies, or other health related studies.

National Biodiesel Board contracted with Lovelace Respiratory Research Institute (LRRI, 2000) for the short-term health effects and toxicology testing mandated for Tier 2. LRRI performed a 13-week subchronic inhalation study in rats of the potential toxicity of biodiesel exhaust emissions. Groups of rats were exposed to diluted biodiesel exhaust emissions at targeted low, intermediate, and high levels concentrations of NO_x and other exhaust gases and compared with air-exposed rats. LRRI reported: "No effects of biodiesel-exhaust-emission exposure were observed in a variety of endpoints including mortality, toxicity, feed consumption, toxicity to the eyes, neurohistopathology, formation of micronuclei (MN) in bone marrow cells, sister chromatid exchanges (SCEs), fertility, reproductive toxicity, and teratology. Endpoints in which effects were caused by biodiesel-exhaust-emission exposure with changes not deemed as biologically significant, included: group mean body weights, non-pulmonary organ weights at necropsy, clinical chemistry, and glial fibrillary acidic protein (GFAP) in the brain." In certain test animals, there was a tendency for increased lung weights and alveolar macrophages, and blackening of the macrophages at the higher exposure level. LRRI reported: "Findings of particles in macrophages and macrophage hyperplasia were judged to be a normal physiologic response to exposure and not a toxic reaction." Basically, the only biologically significant biodiesel exhaust exposure effect was a small effect in lungs at the high exposure level.

The mutagencity of biodiesel exhaust has been evaluated and compared with baseline diesel exhaust. Mutagencity is typically measured using the Ames Assay test that detects reverse mutations in a series of Salmonella typhurium tester strains that carry mutations of histine, which is needed for bacteria growth. A rat liver extract is added as part of the test to simulate the effect of metabolism, as some compounds are not mutagenic themselves, but their metabolic products are.

Several studies of mutagencity have been conducted by researchers in Europe. The Motor Test Center (MTC) in Sweden conducted several chassis dynamometer test programs where unregulated emissions were measured (Gragg et al. 1994, 1998). Tests on a Scania bus showed that mutagencity for the B100 was substantially lower than that for the CARB-like fuel, although the mutagencity for the Fischer-Tropsch like fuel was lower than that for the B100. On a Volvo bus, the Fischer-Tropsch like diesel had slightly lower mutagenicity compared to the B100.

Bünger et al. (1998; 2000a,b; 2006; Krahl et al. 2001; Schröder et al 1999) have conducted several studies of the mutagencity of rapeseed oil methylesters (RME) and soybean oil methylesters (SME) compared to a low-sulfur diesel and a conventional diesel fuel. Comparisons with a low sulfur diesel fuel (LSDF) and RME and SME showed that the LSDF typically has a much lower mutagenicity than the conventional diesel fuel, but that RME and SME provide the lowest mutagencity. These researchers suggested that the results provide an indication that both fuel sulfur and aromatics are important for mutagencity, since lower fuel sulfur in the diesel fuel reduces mutagencity, but still lower mutagencity is found for the biodiesel fuels which contain negligible sulfur and aromatics.

A few studies have also investigated the cytotoxicity of biodiesel exhaust. Bünger et al. have conducted studies of the cytotoxicity of biodiesel compared with diesel exhaust using an assay test with mouse fibroblasts (L929). For cytotoxicity tests on passenger car exhaust, no significant difference in cytotoxic effects was found between the fuels in any of the three vehicle cycles, although the toxicity of the RME exhaust was slightly higher in the FTP-75 (Bünger et al., 1998). In another study, Bünger et al. (2000b) found fourfold stronger toxic effects on mouse fibroblasts at “idling” but not at “rated power” than diesel fuel extracts. In tests where rat lung slices were exposed to diesel exhaust, total glutathione (GSH) showed larger decreases for RME than diesel exhaust, indicating a higher level of this cytotoxicity (Le Prieur et al. 2000). At the same time, an apoptotic phenomenon related to inflammatory response was prevented or significantly reduced for RME blends compared with straight diesel exhaust (Le Prieur et al. 2000; Bion et al. 2002).

One human study was also performed in Europe involving 763 truck drivers exposed to exhaust fumes of both biodiesel and diesel fuel (Hasford et al., 1998). The drivers were provided a questionnaire and in general fewer health complaints were reported for the RME exhaust relative to the diesel exhaust, although some participants did report a “French fry” oder for the bioidesel exhaust fumes. Medical tested did not show any significant differences in lung function for the workers exposed to RME vs. conventional diesel exhaust.

5.18 Summary of Emissions Results

The US EPA’s comprehensive review of emissions studies and reports is one of the primary sources utilized to characterize the emissions impacts of biodiesel. Their results are summarized below. The EPA characterized emissions of hydrocarbons, carbon monoxide and particulate matter as reduced over 10% while emissions of nitric oxides are increased about 2% when soy-based biodiesel is added to petroleum base fuel. However, there are a number of caveats in the EPA report. Most important is that their analysis is based on engines mounted in a laboratory and not engines mounted in vehicles. The EPA states that there is a difference in their analysis for engines in vehicles, one that they cannot define with existing data. Another, important data gap is that the EPA cannot make projections of the changes in NO_x emissions for non-road applications.

Regulated Pollutant	% Change in Emissions for Soy-based B20
NO_x	+ 2.0%
PM	- 10.1 %
HC	- 21.1 %
CO	- 11.0 %

Table 5-2 Emission Impacts of B20 vs. an Average Base Petrodiesel

In addition to the EPA’s draft report, this report reviewed many other expert reports that discussed effect of testing conditions and fuel properties on the emissions from compression ignition engines. With B20, measurements almost always show significant benefits for CO and PM, but results for NO_x are not as clear. With soy-based B20, the NO_x usually increases about 2 to 3%. NO_x increases for yellow-grease based B20 tend to be smaller than those for soy-based biodiesel. The increases at this level are hard to measure so sufficient repetitions are needed to determine statistically significant effects at these levels. Recent work has also shown that the emissions impact of biodiesel is a function of load, with the general trends of higher NO_x emissions being stronger at higher loads. The NO_x increase will disappear with the installation of

NO_x aftertreatment control strategies that will be implemented on new engines in upcoming years.

Included in the expert review were a number of reports by NREL, the federal laboratory responsible for the information about renewable fuels, including biodiesel. NREL's most extraordinary report showed that even with a 100% changeover of all heavy-duty trucks in the Los Angeles Basin from #2 diesel to B20, ozone levels will not measurably increase. Their conclusion is rather striking and informative.

In considering the potential impacts of biodiesel on emissions in Caltrans equipment, the comprehensive biodiesel study being conducted by CARB in support of the upcoming Low Carbon Fuel standard will provide important information. This study will provide the basis for fuel formulations that will be developed for the mitigation of the biodiesel NO_x increase that will be implemented throughout the State. Given that biodiesel emissions impacts are also a function of engine load/operation, it is suggested that Caltrans also conduct some studies directly of the emissions impact of biodiesel in Caltrans equipment and applications. This will provide a more direct measure of the actual impact that can be anticipated under typical use conditions for Caltrans vehicles and equipment.

6 Task 2: Demonstration Project

6.1 Site Description and Demonstration Set-up

The objective of this demonstration is to provide a pilot scale implementation of biodiesel into the Caltrans fleet. The demonstration is anticipated to be a prelude to full implementation of biodiesel blends for diesel vehicles throughout the entire Caltrans fleet.

6.1.1 Site and Duration

The demonstration was held at the Indio, CA Sub-Shop of the Division of Equipment – Shop 8. This site was selected, in part, due to its close proximity to one of the larger distributors/manufacturers of B100 in California.

The demonstration began in February of 2007 and remained active for over a year. During this period, vehicles in the Indio fleet were fueled on B20 and operated over their typical driving conditions. The primary period of experimental data collection and UC Riverside oversight was during the 6 month period between February 2007 and the end of July 2007. At the end of this 6 month period, it was decided to continue the use of biodiesel at the facility to see if any issues were experienced with the biodiesel that might not have been experienced during the primary demonstration period.

6.1.2 Vehicles/Equipment

The Indio site has approximately 21 diesel vehicles and/or pieces of equipment. A list of diesel vehicle/equipment at the site is provided in Table 6-1. This list is based on the vehicles/equipment stationed at the site at the time the demonstration was initiated. The vehicles represent a range of applications including construction equipment, utility vehicles, and dump trucks. The vehicles range in model year from 1986 to 2003. An attempt was made to obtain a vehicle equipped with a diesel particulate filter (DPF), but no such vehicles were available for use at the site during the demonstration period.

Table 6-1. List of Equipment at the Indio Equipment Division Site

	District	Cost Center	Mtce Class	ID	Description	Year	Mileage
1	8	741	907	0090052	PICKUP W/A/C DIESEL	1995	185316
2	8	741	3322	335291	DUMP BODY W/SPREADER	1992	101832
3	8	741	3323	335618	DUMP BODY W/PLOW & SPREADER	1993	143069
4	8	741	3323	337208	DUMP BODY W/PLOW & SPREADER	1999	79234
5	8	741	3323	338735	DUMP BODY W/PLOW & SPREADER	2001	49470
6	8	741	4700	475661	TRUCK TRACTOR	1993	110257
7	8	741	36301	3634434	GRADER-6 WHL DR W/ PLOW 150 HP	1986	6622
8	8	741	41870	4185819	LOADER FRONT END 3 CU YD	1992	2217
9	8	741	56808	5685027	SWEEPER CONV 3.4 CY DIESEL	2003	2346
10	8	741	61126	6115170	TRAILER SEMI TANK 3001-7000 GAL.	1989	2802
11	8	744	930	90478	UTILITY BODY DIESEL	1999	109130
12	8	744	930	98298	UTILITY BODY DIESEL	2001	117620
13	8	744	2350	235431	CARGO BODY W/HOIST 12FT DIESEL	1992	76473
14	8	744	3384	338747	TRASH COMPACTOR 16 CY REAR LOAD	2001	34774
15	8	744	3398	334193	FENCE REPAIR	1987	271869
16	8	744	4794	478615	DIGGER DERRICK 4WD	2001	13230
17	8	744	10930	1098375	UTILITY BODY DIESEL	2001	80617
18	8	744	11151	1114972	CARGO BODY W/O HOIST W/PLOW DSL	1990	133695
19	8	744	41846	4184643	LOADER FRONT END 1-1/2 C.Y.	1986	2598
20	8	744	59218	5926870	TRACTOR WHEEL 120 HP W/2 MOWERS	1995	2317
21	8	744	59218	5927447	TRACTOR WHEEL 120 HP W/2 MOWERS	1997	1810

The demonstration vehicles provide service over the main highways in the Coachella Valley area, including Interstate 10 between route 62 and Dillon Road, Highway 111 south of Rancho Mirage, and highways 62, 74 to Pinyon Pins, 86, and 86S. The typical operation route for the demonstration vehicles is driving between 15-30 miles to a job site, performing work at the site, and returning to the Indio maintenance yard. The routes are generally flat, with the exception of ~1-2 days per month when work in performed on highway 74. The service area is shown in Figure 6-1.

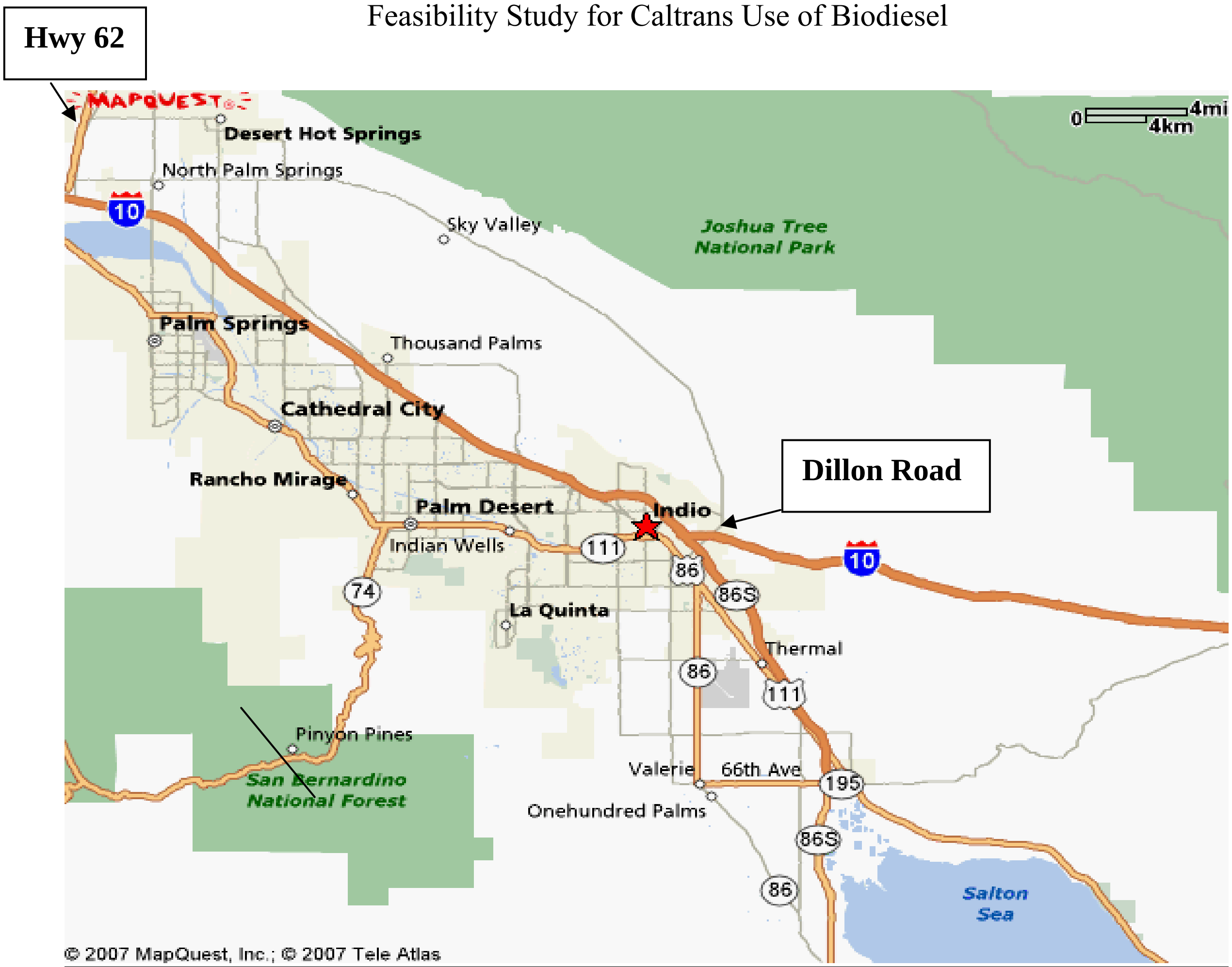


Figure 6-1. Service Area and Location of the Caltrans Indio Maintenance Yard

6.1.3 Fuel and Fuel Delivery

The fuel for this demonstration project was initially provided by Imperial Western Products (IWP) of Coachella, CA during the initial 6 months of the demonstration, where the fleet was actively monitored. IWP provided B20 delivered to the Indio facility at a price that was $0.15 higher than that of typical CARB ultra-low sulfur diesel (ULSD).

IWP performed a subset of analyses with every batch fuel and provided a certificate of analysis (COA). The fuel parameters analyzed each batch include free and total glycerin, water and sediment, cloud point, acid number, visibility, flashpoint, sulfur, and Carl Fischer moisture. The COAs for each batch were be maintained. Additionally, IWP provided samples of the B20 fuel and the B100 for each batch of fuel that is delivered.

The biodiesel was delivered to a 4000 gallon refueling tank that is located on-site in the Indio yard, as shown in the Figure 6-2. The fuel filter for the 4000 gallon tank was changed prior to beginning the refueling with biodiesel. The water level in the tank was checked with the in-tank monitoring system and was found to be at 0.8” out of 82” or approximately 14 gallons out of the 4000 gallon tank. The fuel level in the tank was brought down to a relatively low level prior to making the initial fuel delivery for the B20 in order to ensure that the fuel beginning used by the fleet would contain only a small residual of typical CARB diesel.

Figure 6-2. Fuel Tank Used at the Indio Maintenance Yard

Preparations and Precautions for the Demonstration Program

Consideration was given to cleaning the fuel storage tank prior to beginning the demonstration. Biodiesel does have some solvent-like properties that can act to clean sediment in fuel tanks or fuel storage areas. This can lead to issues with the clogging of fuel filters, although this is not expected to happen in most cases. Cleaning of the fuel storage tank and the vehicle fuel tanks is the most comprehensive method for eliminating any potential fuel filter problems. Since the goal of this demonstration was to provide guidance to Caltrans in the potential implementation of biodiesel to a larger fraction or the entire Caltrans fleet, no special precautions were taken with respect to cleaning of fuel storage tanks, vehicle fuel tanks, or accelerated changes of fuel filters.

Discussions were held with the maintenance supervisor prior to beginning the demonstration program. Again, the solvent-like qualities of the biodiesel were the most important areas of emphasis. It was emphasized that extra care and checks should be made of the fuel filters, as possible. It was requested that fuel filters be kept if they showed higher than normal sediment buildup. Biodiesel can also have an impact on the integrity of fuel lines, predominantly for older (pre-1994 model year) vehicles. It was suggested that the fuel line integrity for older vehicles be checked at scheduled maintenance periods after the implementation of the biodiesel fuel. Again, this was not expected to be a significant issue, particularly since pure biodiesel (B100) was not being used.

6.2 Demonstration Results

One of the goals of the demonstration program was to gather data to allow evaluation of the success of the demonstration program. Data collection efforts out of necessity were designed to minimize all impacts to the typical fleet operation. In most cases, the data collected and analyzed was part of existing data collection streams.

6.2.1 Fuel Records/Usage/ Deliveries

Fuel was delivered to the site 4 times during the course of the initial 6 months of the demonstration. In total, 10,807 gallons of B20 were utilized during that time period.

An attempt was made to obtain more detailed fuel mileage and usage records for each vehicle in the fleet. UCR worked with the fleet to obtain the most detailed records possible using the Caltrans Pre-operation checklist for each vehicle. This book is filled out each day the vehicle is used and hard copies are maintained on site. Initially, it was thought that electronic records maintained under the "Ring" system would be able to provide the vehicle mileage between fuel stops as well as the total fuel use per vehicle. A closer examination of the "Ring" records, however, indicated that the mileages were correct for only a limited number of vehicles, hence it was determined that these records would not be suitable.

While some fuel mileage records were collected throughout the course of the program, the data available from the pre-operation checklist was sporadic at best and was insufficient to show any significant fuel use trends. The necessary information on miles travelled between fill ups or amount of fuel used during a day or between fill ups was only available for part of the collected records. Based on the limited records available, fuel mileage was often found to have unrealistic values or showed large swings in mileage between different days. Based on these results, it must be stated that the fuel mileage records were not sufficiently reliable to allow an evaluation of any changes in fuel mileage over the course of the demonstration period. It can be noted, however, the no significant changes in fuel mileage were noted by the drivers during the normal course of daily operations.

6.2.2 Fuel Blending and Density

Toward the end of the initial 6 months of the demonstration project, a field sample was collected from the fuel tank. The sample was collected near the end of the initial 6 month period since it was assumed that the tank would be essentially flushed of the initial low levels of diesel fuel that were in the tank at the beginning of the program. Two samples were pulled from the tank: one sample from the top and one sample from the bottom of the tank. The samples were analyzed at UC Riverside to determine if there are any significant differences in density at various points in the tank. Such differences in density could be indicative of non-uniform blending and may be further investigated. The samples were found to have specific gravities of 0.840 for the top of the tank and 0.8405 for the bottom of the tank, indicating there was a uniform mix of B20 in the fuel tank.

6.2.3 Maintenance Records

Caltrans keeps several types of data records on the maintenance of its vehicles. Records are maintained in hard copy in the “Permanent Equipment Maintenance Record” that is maintained with each of the vehicles. These maintenance records include the type of repair and the date on which the repair was performed. Electronic records are maintained for each vehicle repair and maintenance job that is conducted. The electronic records include information such as the number of labor hours, parts cost, and total cost, in addition to the type of repair. A sample of the electronic records is provided in Appendix H. No significant changes were made in the keeping of the maintenance records, other than the addition of comments if the problem being addressed appears to be an artifact of the biodiesel usage. In such as case, the problems were generally discussed directly with maintenance and repair shop.

In addition to the standard maintenance records, the drivers/mechanics will be given a malfunction log sheet. This malfunction log sheet will be used for each incident where a malfunction is identified for a vehicle operating on the biodiesel blend. The malfunction log provided a more comprehensive and uniform assessment of such factors as the condition under which the malfunction is observed, the type of driving problem observed, and the severity of the problem. During the course of the 6 month active demonstration program, no records were obtained in the maintenance log.

6.2.4 Operator Survey

The drivers were each given a survey to qualitative evaluation their experiences with the fuel. The survey will include issues such as drivability, power, and startability. The driver’s survey is provided in Appendix I. A total of 11 drivers took the survey. In general, the survey results indicated no significant problems with the use of biodiesel or the operation of the vehicle when it was running on biodiesel. In one case, a driver indicated that he refueling problems and startability problems with a vehicle operating on biodiesel, although not elaboration was given as to the specific nature of the issue. Additionally, this driver indicated that the operability and startability of the vehicle was comparable to that of diesel fuel. One driver also indicated that he felt the performance and operability of the vehicles was better on the biodiesel. Overall, the operator survey data indicate that the performance of the vehicles on biodiesel was comparable to that on regular diesel fuel.

7 Biodiesel Fleet Survey

A survey was conducted of various biodiesel fleets utilizing biodiesel. Information was also gathered on fueling sites in the California area. These sources of information can both be used to better understand the practical implementation of biodiesel into a standard fleet operation within Caltrans. Information on other fleet demonstrations is also covered under the literature review in section 3.8.

7.1 Fleet Surveys

A survey was conducted of a subset of fleet that utilizes biodiesel throughout the country. For this project, the survey included national park sites as well as a few other users of biodiesel such as the US Postal Service. The surveys to the fleet managers included a number of different questions on topics such as cost, blend level, types of engines/vehicles used, amount of gallons used, and any maintenance or other operational issues that were identified.

7.2 Fleet Survey Results

The survey results for the fleets that responded are provided below in Table 7-1. The fleet usage ranged in size from approximately 80 to 6000 gallons per week. Two of the larger fleets, Yellowstone and the US Postal Service, were also relatively long term users, with use dating back to 1995. Some incidences of filter plugging and fuel gelling were recorded, although in most cases these issues appeared to be shorter term issues. The postal service was the only fleet that reported a persistent problem with plugging on one specific type of Mack truck fueling system. The postal service also noted problems with fuel injector wear and sludge in the valve train. Biscane reported more frequent seal and fuel injector failures, although this fleet was using B100 instead of a biodiesel blend. Biscane also report that the day tank floats stuck on the engine. The fuel prices were higher for the biodiesel in all reported cases, although there was quite a bit of variation in the amount of the increase. The fuel price data was based on data collected in late 2006 with many regional differences between the fleets. With the continual fluctuations in fuel prices, particularly with respect to CARB-certified fuel, fuel pricing would likely need to be assessed on a case-by-case or fleet-wide basis to determine the actual cost differential for biodiesel use.

Table 7-1 Survey Results from Biodiesel Fleet Operators

	Assateague Island, MD	Biscayne, FL	National Capitol, DC	Pictured Rocks, MI
Ever used?	Yes	Yes	Yes	Yes
Ever considered?				
Why not?				
When did you start?	2002	2004	1998	2000
Feedstock?	Don't know	Rape Methyl Ester, Yellow Grease	Soy Methyl Ester	Soy Methyl Ester
Petroleum component?	#2 year round	None	#2 diesel	Blend of 50% #1 + 50% #2
How is it blended?	At terminal + "splash mixed"		At terminal + "splash mixed"	Blended in storage tanks
Changes to storage?	No	Keep less in stock.	N/A	No
Cold storage?	No changes needed.	No changes needed.	No changes needed	Yes
Types of engines	All diesel in fleet	Other diesel equipment	All diesel engines in fleet	All diesel engines in fleet
Gal/week	Est. 250	450	200	80
Price difference?	$1.59/gal for B20	$1.00/gal		$0.15
Filter problems?	None	Filters plugging at the engine	Unusual residue: gel	Unusual residue: sludge
Filter problems persists?		Abated	Not Yet	One time occurrence
What kind of filters?		Multiple types of filters	Don't know	One type: paper
Weather problems?	None	None	None	None
Power difference?	No	Less	No	More
Change in fuel mileage?	Not measured	Not measured	No change noted	Not measured
Fuel system problems?	Not monitored	Seals+injectors fail more frequently	gel from HUM bugs	Not monitored
Engine oil analysis?	No changes noted.	No changes noted	No changes noted	No changes noted
Oil change interval?	No change.	Only when main engine seals fail	No	No
Any other problems?	No	Day tank floats stick on engine	Yes	No

	Grand Teton, WY	Yellowstone, WY	United States Postal Service	Las Vegas Clean Cities
Ever used?	Yes	Yes	Yes	Yes
Ever considered?				
Why not?				
When did you start?	2000	1995	1995	2001
Feedstock?	Soy Methyl Ester	Other	Don't know	Soy Methyl Ester
Petroleum component?	#1 (Nov-Feb), Blend 50% #1 + 50% #2	None		#2 Year round
How is it blended?	At terminal + "splash mixed"	At terminal + "splash mixed"	Don't know	At terminal + "splash mixed"
Changes to storage?	Monitor fuel storage tanks + fuels	No	Yes	
Cold storage?	No changes needed	No changes needed	No changes needed	No changes needed
Types of engines	All diesel engines in the fleet	All diesel engines in fleet	Delivery vehicles	All diesel engines in fleet
Gal/week	1300	4000	4000	6000
Price difference?	$0.18	None	10% more	$0.08
Filter problems?	No Problems	No problems	Filters plugging at the engine	No problems
Filter problems persists?			persists	
What kind of filters?			One type: Mack Tractor Fuel System	
Weather problems?		None	None	None
Power difference?	Less	No	No	More
Change in fuel mileage?	Increase of 0.2 MPG on Kenworth ECMs	Zero change in MPG	No change noted	Increase of .6 MPG
Fuel system problems?	Routinely monitored, but no differences	Routinely monitored, but no difference	Fuel injector wear	Routinely monitored, but no difference
Engine oil analysis?	No changes noted	No changes noted	No changes noted	No changes noted
Oil change interval?	No	No	No	No
Any other problems?	No	No	Yes	No

7.3 Biodiesel Refueling Sites within California

Information was gathered on fueling sites throughout California. The availability of biodiesel outside of the fleet operating yard could be of use in situations where fuel outside the yard was necessary. While this is of interest, it would not be the significant factor in considering biodiesel use, since vehicles could also be filled with standard diesel fuel in situations where biodiesel fuel was not available. A table of the biodiesel fuel sites in California is presented below.

7.4 National Park Fleet Vehicle Records

As part of this program, UC Riverside obtained a listing of all vehicles being operated in national parks and at national park sites along with contact information. Aside from the national parks listed above, the following national parks or sites operate at least one vehicle on biodiesel: Big South Fork NRRA, TN, Channel Islands, CA, Everglades, CA, Glacier, MT, George Washington Memorial Parkway, VA, Harpers Ferry, WV, Mammoth Cave, KY, Mount Rainier, WA, National Capital Park Region, DC, Redwood, CA, Scotts Bluff, NE, Sleeping Bear Dunes, MI, Voyageurs, MN, and Yosemite, CA. This information will be provided to Caltrans along with the submission of the final report.

Table 7-2 Biodiesel Refueling Stations in California

Name	Location	Contact	Phone	Blend	Notes
Baker Commodities, Inc.	4020 Bandini Boulevard Los Angeles, CA 90023	Fred Wellons	323-268-2801		biodiesel plants
Bay Area Diablo Petroleum	3575 Pacheco Blvd Martinez, CA 94553	Jack Bene	925-372-5406	B100	Any Blend. Open 7-4 M-F.
BioFuel Oasis	2465 - 4th St. Berkeley, CA 94710	Gretchen Zimmerman	510-665-5509	B99	Sun, Tue, Thur. 4-8pm, Fri & Sat 10-
Eel River Fuels, Inc	220 East Highway 20 Upper Lake, CA 95485	Woody	707-275-2045	B99	7 Days a week; cash/credit
Eel River Fuels, Inc	3371 North State Street Ukiah, CA 95482	Ken Foster / Al Banta	707-462-5554	B99	24/7, All Major Credir Cards
Golden Gate Petroleum	421 J Street Arcata, CA 95521	Patrick Okeefe	707-826-9268	B20	Credit/Cash & Open Mon-Sun 6am -9pm
ITL, Inc.	8330 Atlantic Ave Cudahy, CA 90201	Mike Rohrer	323-562-3230	B20	Premium B20 at the pump – cash/credit
Imperial Western Products	PO Box 1765 Indio, CA 92202	Bob Clark	760-398-0815		
McCormix Corporation	22 N. Calle Ceasar Chavez, Santa Barbara, CA 93117	Ken Olsen	805-963-9366	B20, B100	6am - 5pm
McCormix Corporation	55 Depot Rd. Goleta, CA 92117	Ken Olsen	805-963-9366	B20	24 hours a day
Mountain Feed and Farm Supply	9550 Highway 9 Ben Lomond, CA 95005	Jorah Roussopoulos	831-336-8876		Mon.-Sat. 9-6 Sun. 10-2
Pacific Biofuel	1601 Jarvis Rd Santa Cruz, CA 95065	Ray Newkirk	831-459-6774	B100	Retail purchasers must call ahead
Renner Petroleum/World Energy	76 Bear Canyon Rd. Garberville, CA 95542		707-443-1645	B20	public/no restrictions
RTC Fuels, LLC	4067 El Cajon Blvd. San Diego, CA 92105	Mike McCallen	619-521-2469	B20	
San Francisco Petroleum	4290 Santa Rosa Ave Santa Rosa, CA 95407	Rod Martin	707-586-2765	B100	
Solar Living Institute	13771 South Hwy 101 Hopland, CA 95449		707-744-2017	B100	M-F 8:30 - 5:30 / Sat/Sun 10-5
T.W. Brown Oil	1457 Fleet Ave. Ventura, CA 93003	Ted Brown, Sr.	805-339-2355	B20, B99	
The Biofuel Station	44440 Highway 101 Laytonville, CA 95454	Kimber or Eric	707-984-6818	B100	M-F 9-5
Toro Petroleum Corp	2109 Fremont St Monterey, CA 93940	James Hill	831-424-1691	B100	
Ventura Harbor Marine Fuel, Inc.	1449 Spinnaker Dr. Ventura, CA 93001		805-644-4046	B100	public
Western States Oil	1790 S. 10th San Jose, CA 95112				open 9-5 M-F; cash or credit card
Weststart	48 South Chester Ave Pasadena, CA 91106	Susan Romeo	626-744-5686		
World Energy Alternatives LLC	408 Broad Ste 11B Nevada City, CA 95959	Graham Noyes	530-478-9196		
Yokayo Biofuels	150 Perry Street Ukiah, CA 95482	Kumar Plocher	877-806-0900	B100	M-F 9-5; Cash, Check, MC/Visa

8 Conclusions and Recommendations

Biodiesel is becoming one of the more promising alternative fuels as California and the nation strive to displace petroleum, develop renewable fuels and reduce greenhouse gas emissions. Caltrans must carefully review many factors, however, before incorporating a new fuel in its fleet. The factors include the issues associated with operability/warranty of the fleet, costs due to the fuel and the impact on the environment. In the context of these issues, this study was designed to provide a complete evaluation of all aspects of biodiesel use to access the feasibility of its use in the Caltrans fleet. This study was separated into three primary areas of research, a literature review, a pilot biodiesel demonstration at a Caltrans facility, and a survey of other fleet users of biodiesel. A summary of the findings of this study are as follows:

- Biodiesel fuel is the most advanced alternative diesel fuel currently available. An ASTM specification has already been developed for biodiesel. In June of 2008, the ASTM committee adopted a modified petrodiesel specification ASTM D975 to include blends of up to 5 volume percent of biodiesel and created a new stand alone specification to handle bends of biodiesel up to 20 volume percent. Biodiesel is also the only alternative fuel in the United States to have successfully completed the EPA's Tier I and Tier II Health Effects testing under Section 211(b) of the Clean Air Act. Tier I testing demonstrated biodiesel's significant reductions in most currently regulated emissions as well as most unregulated emissions. Results of Tier II testing showed that biodiesel's emissions had a non-toxic effect on human health. Biodiesel also has a quality control/assurance program, BQ9000, for producers and distributors.

- Biodiesel use continues to rise nationwide, with a total of 450 million gallons produced in 2007. DOE estimates indicate that in total there is enough feedstock to supply about 1.9 billion gallons of biodiesel per year, which represents approximately 5% of the on-road diesel used in the US.

- Biodiesel can be made from a variety of different feedstocks. Soy-bean oil is the most popular feedstock in the United States, followed by yellow-grease or recycled cooking grease, with other feedstocks such as palm oil (Asia) and rapeseed oil (Europe) more common in other areas. Biodiesel receives a tax credit that equates to one penny per percent of biodiesel in a fuel blend made from agricultural products like vegetable oils or other first-use materials, or one-half penny per percent of biodiesel used in a fuel blend made from recycled or second-use oils.

- Biodiesel is relatively easy to implement into existing fleet operations since it can be utilized with the existing diesel fuel infrastructure and in existing diesel engines. Biodiesel does have some solvent-like properties that can act to clean sediment in fuel tanks or fuel storage areas or compromise the fuel line integrity for older vehicles. For normal use of B20 blend, it is expected that the incidences of these problems will be minor. Our recommendation is to utilize some additional precaution in fuel filter maintenance and related issues, but not to implement special practices that would be expensive on a fleet-wide basis. Additionally, fuel surveys over the last several years have shown that biodiesel fuel quality can vary significantly, although it is improving.

The BQ9000 standard initiated by the biodiesel industry is an important step to standardizing the quality of the biodiesel produced around the country. It is strongly recommended that Caltrans utilized to extent possible producers or distributors that are BQ9000 certified.

- Biodiesel can have an impact on exhaust emissions. Most studies show a reduction in CO, HC, and PM compared to more traditional diesel fuel. The potential for biodiesel to impacting NO_x emissions remains an issue in California, although the increases are smaller (2-3%) than the benefits typically seen in the other pollutants. Although there are some generally observed trends for biodiesel, the impact of biodiesel on emissions depends on the testing load, base fuel of comparison, and application. The NO_x increase will disappear with the installation of NO_x aftertreatment control strategies that will be implemented on new engines in upcoming years.

- Caltrans should follow the development of CARB's ongoing comprehensive study of biodiesel emissions. This study will provide the basis for fuel formulations that will be developed for the mitigation of the biodiesel NO_x increase that will be implemented throughout the State. It is also suggested that Caltrans also conduct some direct studies of the emissions impact of biodiesel in Caltrans equipment and applications, since the emissions impacts are a function of engine load and operation. This work is currently being carried out in a follow on Caltrans study.

- In the demonstration pilot program, biodiesel (B20) was utilized for a period of over one year with no adverse impacts on normal operation. No adverse maintenance issues were identified in this period. The fuel was utilized in a variety of ambient conditions from desert heat to colder mountain weather operation. Equipment operators and drivers all indicated that performance was comparable to that of typical diesel fuel.

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Appendix A –

Caltrans Directive to Use Alternative Fuels

State of California
DEPARTMENT OF TRANSPORTATION

Business, Transportation and Housing Agency

Flex your Power!
Be energy efficient!

Memorandum

To: DISTRICT DIRECTORS
DEPUTY DISTRICT DIRECTORS
DIVISION CHIEFS
DISTRICT EQUIPMENT MANAGERS

Date: July 6, 2006

From: LISA M. KUNZMAN
Chief
Division of Equipment

Subject: Use of Alternative Fuels

In an effort to comply with target recommendations identified in *California State Vehicle Fleet Fuel Efficiency Report of 2003*, the Division of Equipment (DOE) is monitoring fuel usage of all alternative fuels. The Department is required to regularly report on its alternative fuel usage to federal and state agencies.

At present there are approximately 2,027 bi-fuel and flexible fuel vehicles actively being used statewide by California Department of Transportation (Caltrans) employees. These units have the ability to operate on gasoline as well as alternative fuels such as liquid propane gas (LPG), compressed natural gas (CNG), and ethanol.

Of particular note are 1,294 LPG/gasoline bi-fuel vehicles. It has been determined through our research that the vast majority of these vehicles are being fueled using conventional gasoline rather than the alternative LPG, although there is an established and extensive network of propane filling stations throughout the State.

We recognize that although alternative fueling sites are available, it is sometimes more convenient to fill these variable fuel vehicles with gasoline rather than lower emission alternative fuels. However, Caltrans has a responsibility to utilize these units to their utmost potential by ensuring they are operated using alternative fuels whenever possible. By doing so, Caltrans will exhibit a notable commitment to improving the environment and will further lessen our dependence on petroleum-based fuels.

An important goal of Caltrans is to demonstrate proactive stewardship in shifting the State's dependency on standard fuel sources. Public Resources Code Section 25722.5 (c) states, *"To the maximum extent practicable, each State office, agency and department that has bi-fuel natural gas and bi-fuel propane vehicles in its vehicle fleet shall use the respective alternative fuel in those*

"Caltrans improves mobility across California"

District Directors, et al
July 6, 2006
Page 2

vehicles." Consequently, all employees who are or will be operating a vehicle with alternative fuel capability are strongly advised to take the necessary steps to use appropriate alternative fuels rather than gasoline. If alternative fuels are not readily available or procuring them will significantly hinder your ability to conduct necessary business, you may opt for and continue to use standard gasoline sources.

Should you have any questions regarding alternative fuel vehicles in general or fueling sites in your area, please refer to the DOE website www.dot.ca.gov/hq/eqsc/altfuel/altfuel.htm or contact your District program equipment manager for additional information.

c: GMallette, Deputy Division Chief, Division of Construction
FRuiz, Statewide Equipment Manager, Capital Outlay Program
LNelson, Statewide Equipment Manager, Division of Maintenance
AMills, Assistant Statewide Equipment Manager, Division of Maintenance
SWhitmore, Operations Chief, Division of Equipment
Shop Superintendents, Division of Equipment

Appendix B:

ASTM D-6751-02 Standard Specification for Biodiesel Fuels (B100) Blend Stock for Distillate Fuels (example only, out of date) Selected properties.

Property*	ASTM Test Method	Limits	Units
Acid Number	D 664	0.80 max.	mg KOH/g
API Gravity	D287		
Btu Content – Net Heating Value	D240		Btu/gal
Carbon Residue	D 4530	0.050 max.	% Mass
Cetane Number	D 613	47 min.	
Cloud Point	D 2500	Report	^{o}C
Copper Strip Corrosion	D 130	No. 3 max.	
Distillation Temperature	D 1160	360 max.	^{o}C
Flash Point	D 93	130.0 min.	^{o}C
Free Glycerin	D 6584	0.020	% Mass
Kinematic Viscosity, 40^{o}C	D 445	1.9 – 6.0	mm^2/s
Phosphorous Content	D 4951	0.001 max.	% Mass
Species Analysis of 6 –8 Esters, 16 –20 Carbon in Length			
Sulfated Ash	D 874	0.020 max.	% Mass
Sulfur	D 5453	0.05 max.	% Mass
Total Glycerin	D 6584	0.024	% Mass
Water and Sediment	D 2709	0.050 max.	% Volume

* Properties that are not common to petroleum distillate fuels

Appendix C –

Structural Formula for Specific Fatty Acids Occurring in Biodiesel

Fatty Acid Name	No. Of Carbons & Double Bonds	Chemical Structure (= denotes double bond placement)
Caprylic	C8	$CH_3(CH_2)_6COOH$
Capric	C10	$CH_3(CH_2)_8COOH$
Lauric	C12	$CH_3(CH_2)_{10}COOH$
Myristic	C14	$CH_3(CH_2)_{12}COOH$
Palmitic	C16:0	$CH_3(CH_2)_{14}COOH$
Palmitoleic	C16:1	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
Stearic	C18:0	$CH_3(CH_2)_{16}COOH$
Oleic	C18:1	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic	C18:2	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Linolenic	C18:3	$CH_3(CH_2)_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Arachidic	C20:0	$CH_3(CH_2)_{18}COOH$
Eicosenoic	C20:1	$CH_3(CH_2)_7CH{=}CH(CH_2)_9COOH$
Behenic	C22:0	$CH_3(CH_2)_{20}COOH$
Eurcic	C22:1	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$

Appendix D –

Summary of Biodiesel Stability Tests and Research in the Stability of Fatty Acids and Lipids

Three of the methods has achieved widespread credibility with The American Society of Testing Methods (ASTM) for petroleum products and are shown below. Likewise the American Oil Chemists Society (AOCS) has recommended methods for measuring the stability of vegetable oils and many recommend one of these methods for biodiesel. A brief description of the bench methods follows.

Oxidation Stability of Distillate Fuel Oil (ASTM D2274) is used to determine the inherent stability of middle distillates through accelerated oxidizing conditions. In this test a sample of oil is heated to 95°C for 16 hours with oxygen bubbling through and the amount of sediments formed is used to estimate the storage stability. This method is used for middle distillate fuels and is included as a test method for DoD's purchase of B-20 biodiesel fuel.

Long Term Distillate Fuel Storage Stability (ASTM D4625) test is used to evaluate the inherent stability of petroleum products. A sample of oil is aged for up to 24 weeks at 43°C. The method is very useful to obtain close correlation to field conditions for storage up to a year and has been shown to estimate storage stability more reliably than other more accelerated tests. However, the method takes too long to be used for quality control.

Accelerated Stability (ASTM D6468) determines the relative stability of a fuel subjected to a thermal degradation process such as fuel used to cool the injectors and returning "hot" to the fuel tank. In the test, filtered fuel is heated to 150°C to accelerate chemical reactions that create fuel degradation byproducts, in the form of insoluble gums and solid particulate matter. Filtering the deposits on a filter pad and comparing the filter pad to a reference characterizes the stability of the fuel.

Oil Stability Index (AOCS Method Cd 12b-92) is used to identify the length of time before the rate of oxidation of a vegetable oil becomes very rapid. A sample of oil is heated to temperatures between 100° and 140°C with air flowing through the sample. This method is reported as one of the best measures of the stability of a biodiesel fuel.

Bates and Fathoni (1991) have provided an excellent literature review of the fuel stability studies with emphasis on diesel oil, but biodiesel is not included. Some biodiesel stability studies in the literature provided support for the selected petroleum test methods. Bondiloi et al. (2002) reported on the usefulness of ASTM 4625 for a number of B100 biodiesel fuels and concluded that the method gave some indication of whether the oils could be stored for a long time but the test took too long. The careful study incorporated the latest changes for ASTM 2274 recommended by Stavinoha and Howell (2000, 1999). Monyem et al. (2000) reported that the ASTM D2274 was not an appropriate test for biodiesel and instead suggested an oxidation test for lipids, CD 12b-92. Prankl and Schindlbauer (1998) reported on the oxidation stability of fatty acid methyl esters as indicated by the Rancimat test method that was subsequently adopted in Europe.

Although no single test method for stability has emerged, it is generally agreed that the results of several simple chemical/physical tests, namely acid number, concentration of peroxides and viscosity correlate well with the accelerated aging test methods. For example, the data of Frame (1997) in the figure below, clearly shows that fuel acid number increases sharply at about the same time that insolubles increase as measured by test method ASTM D4625

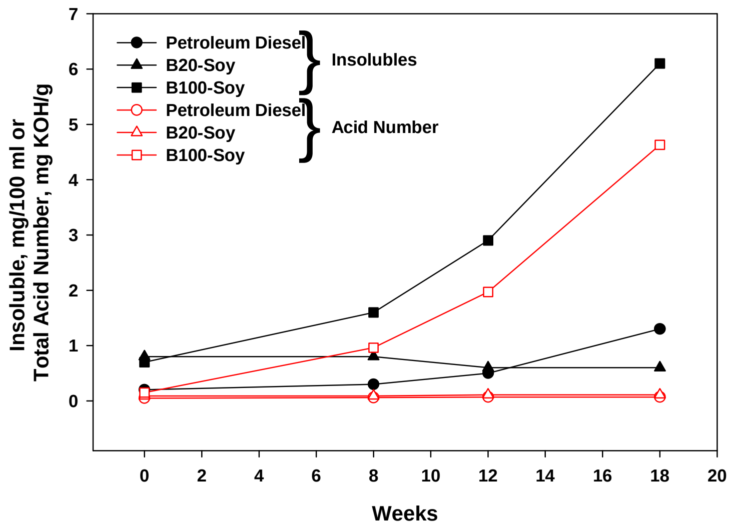

Figure D-1. Results of ASTM D 4625 test from Frame (1997)

In earlier work, Canakci et al. (1999) reported on their research to understand the oxidation of biodiesel fuel, diesel #2 fuel and mixtures with oxygen, temperature and metals as variables in controlled laboratory conditions. They found oxygen, biodiesel, natural antioxidants and copper all affected the aging of the biodiesel. Also while the peroxide value, acid value, and viscosity increased at the same rate with increased oxygen; however, the rates varied as temperature was raised suggesting a change in the intrinsic kinetics and pathways. In a companion article, Monyem et al. (2000) describes testing under simulated in-use conditions to determine the impact of oxidized biodiesel on an engine's fuel system. References provided in Canakci et al. (1999) indicate that many investigators did not agree on the effect of metals on the instability to biodiesel. For example, as seen in the figure below, their research showed that copper accelerated the oxidation rates.

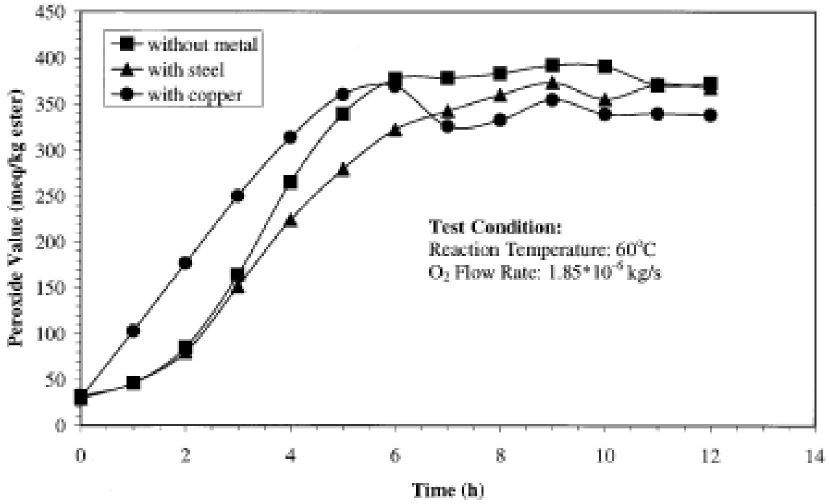

Figure D-2. Effect of Metals on the Peroxide Number

In another project, the National Biodiesel Board (2002) reports on the effect of metals on storage stability was investigated by repeating ASTM D 4625 and placing metal specimens in the fuel aging containers with pure biodiesel, pure petrodiesel, and a 20% biodiesel blend. Steel, copper, and aluminum were tested individually, as well as a mixture of lead, tin, and zinc. Sediment formation with biodiesel and biodiesel blends was unaffected by the presence of steel and aluminum. The mixture of lead, tin and zinc produced severe sediment formation in all samples containing biodiesel. Copper slightly increased formation of sediment in the neat biodiesel. Reasons for the results were not obvious.

Lipids and Fatty Acids

While earlier references reported on the oxidative stability results for biodiesel fuel, there is a companion literature that is more exhaustive on the basic chemical reaction pathways and kinetics of lipid oxidation and autoxidation and thermal degradation in foods and biological systems. Work that was started in the 1980's by the USDA (Department of Agriculture) such as Bagby et al. (1987) is often not referenced by the people working on fuels. Even the nomenclature is different. One group uses biodiesel and the other uses lipids. Lipids are biological molecules that are insoluble in aqueous solutions and soluble in organic solvents. Fatty acids are a type of lipid, specifically long-chain mono carboxylic acids. The numbering of carbons in fatty acids begins with the carbon of the carboxylate group and there is always an even number of carbon atoms from C12 to C24. Fatty acids that contain no carbon-carbon double bonds are termed saturated fatty acids; those that contain double bonds are unsaturated fatty acids. The numeric designations used for fatty acids come from the number of carbon atoms, followed by the number of sites of unsaturation (palmitic acid is a 16-carbon fatty acid with no unsaturation and is designated by 16:0). The site of unsaturation in a fatty acid is indicated by the symbol Δ and the number of the first carbon of the double bond (palmitoleic acid is a 16-carbon fatty acid with one site of unsaturation between carbons 9 and 10, and is designated by $16{:}1^{\Delta 9}$).

A quick scan of recent literature indicates that the work on lipids is relevant to the search for answers in the differing results on the stability of biodiesel. Further, the work on lipid oxidation can provide insight into the proper design of experiments and the selection of analytical methods since the lipid scientists often focus on following certain reaction pathways or reactive molecules at the molecular level rather than on the measurement of a bulk property. One example of this research includes the work of Matikainen et al. (2003) who reported on the determination of the degree of oxidation of methyl linoleate and methyl linolenate at room temperature, both key molecules in biodiesel. In another investigation, Nakatani et al. (2001) established a model substrate oil to study antioxidant activity by the Oil Stability Index (OSI) method. Specifically, he measured OSI values for methyl linoleate with different concentrations (5-100%) in silicone oil. Soriano et al. (2003) studied the ozoneation of sunflower oil with spectroscopic techniques. Still another collection of related work can be found in Frankel's (1998) book: *Lipid Oxidation*.

The point is that the lipid oxidation science is mature and relevant to the biodiesel problems. For example, those knowledgeable of lipid oxidation are likely to follow known reaction mechanisms on the acid hydrolysis of single methyl esters or the acceleration caused by trace amounts of copper ions or the red-ox issues associated with copper/cupric ions. They are also interested in the stabilization of foods against oxidation either at room temperature or elevated temperatures. Studies follow natural antioxidants and their fate as the temperature is raised when used as frying oil. However, natural antioxidants such as tocopherol that is used in food may not be the most cost effective antioxidant for fuel applications. CheMan and Mighani (2001) followed the molecular weight distributions of degradation products of frying oils using new analytical methods, such as high-performance size-exclusion chromatography (HPSEC) with viscometric (VIS)/refractometric (RI) detection. It appears that lipid science has developed many techniques that would be most helpful when applied to the questions of biodiesel stability.

One area of overlap between the fuels and lipid scientists is the detailed analysis of the various biodiesel fuels and their properties. Recently, Kinast (2003) reviewed the property changes in fuel properties as it related to the chemical compounds in various biodiesel fuels. Kinast points out that the methyl esters follow some patterns. The soy, canola (rapeseed), and two yellow grease ME are mostly oleic and linoleic acid (C_{18}, one and two double carbon bonds), while the two largest components of the lard, edible tallow, and inedible tallow ME are oleic and palmitic acid (C_{18}, one C:C bond, and C_{16}, saturated).

	Soy ME	Canola ME	Lard ME	Edible Tallow ME	Inedible Tallow ME	LFFA Yellow Grease ME	HFFA Yellow Grease ME
Lauric $C_{12}H_{24}O_2$	(trace)	(trace)	0.12	0.06	0.08	(trace)	(trace)
Unknown	(trace)	(trace)	(trace)	(trace)	0.05	(trace)	(trace)
Myristic $C_{14}H_{28}O_2$	0.09	0.07	1.86	2.91	2.08	(trace)	1.08
Unknown	(trace)	(trace)	0.09	1.57	1.18	(trace)	(trace)
Palmitic $C_{16}H_{32}O_2$	10.54	5.25	24.49	24.34	23.93	11.53	17.3
Unknown	(trace)	(trace)	(trace)	(trace)	(trace)	0.18	(trace)
Palmitoleic $C_{16}H_{30}O_2$	0.13	.22	2.80	3.44	2.79	(trace)	2.23
Unknown	0.14	.23	0.89	3.01	2.34	(trace)	0.97
Stearic $C_{18}H_{36}O_2$	3.75	2.46	14.39	19.10	19.54	13.36	9.54
Unknown	(trace)	(trace)	(trace)	(trace)	(trace)	(trace)	(trace)
Oleic $C_{18}H_{34}O_2$	23.18	58.09	38.32	40.23	38.54	60.67	45.28
Unknown	(trace)	(trace)	0.07	0.24	0.24	12.02	(trace)
Linoleic $C_{18}H_{32}O_2$	48.92	21.79	13.44	2.58	6.43	0.62	14.48
Unknown	7.08	6.63	0.70	0.32	0.52	(trace)	0.57
Linolenic $C_{18}H_{30}O_2$	1.16	0.41	0.33	0.33	0.32	(trace)	1.3
Unknown	1.47	(trace)	(trace)	(trace)	(trace)	(trace)	(trace)
Arachidic $C_{20}H_{40}O_2$	0.24	1.04	0.45	0.29	0.34	0.41	1.06
Unknown	0.39	0.12	0.10	0.51	0.18	(trace)	(trace)
cis-eicosanoic $C_{20}H_{38}O_2$	0.32	1.57	0.67	0.51	0.46	0.21	1.33
Unknown	1.76	0.80	0.86	0.36	0.62	0.49	2.58
Behenic $C_{22}H_{44}O_2$	0.12	0.37	0.18	0.05	0.06	0.32	0.75
Unknown	0.10	(trace)	(trace)	(trace)	(trace)	(trace)	1.54
Erucic $C_{22}H_{42}O_2$	0.08	0.37	0.06	0.09	0.06	(trace)	(trace)
Unknown	0.52	0.42	0.19	0.05	0.25	(trace)	(trace)
Nervonic $C_{24}H_{46}O_2$	(trace)	0.18	(trace)	0.00	(trace)	0.17	(trace)

Table D-1. Gas Chromatographic Analyses of Fatty Acids

Interestingly, his detailed compound analyses show many molecules that the food scientists have studied for years both at room and at elevated temperature, and with/without antioxidants. Lipid scientists have measured the pathways for the oxidation of many of these compounds neat or in mixtures and their knowledge should be helpful in developing tests and strategies for dealing with biodiesel stability. The point is that the tools and approaches used by the lipid scientists allow a fresh look at the intrinsic mechanisms of instability and micro measurement rather that a macro measurement like weight, viscosity or color of a deposit that are used by the fuel scientists. Their approach offers the potential for setting specifications on molecules that are suspected to be culpable in instability processes; for example, linolenic acid.

Appendix E –

Military Purchase Spec, Biodiesel (B20) (DESC JAN 2004)

NOT MEASUREMENT SENSITIVE
A-A-59693A
JANUARY 15, 2004
SUPERSEDING
A-A-59693
September 7, 2001
COMMERCIAL ITEM DESCRIPTION

DIESEL FUEL, BIODIESEL BLEND (B20)

The General Services Administration has authorized the use of this commercial item description, for all federal agencies.

1. SCOPE. This commercial item description covers a biodiesel fuel blend containing 20 percent (%) biodiesel, with the remainder being low-sulfur diesel fuel oil. This fuel blend, hereafter referred to as B20, is intended for use in all non-tactical diesel fuel-consuming vehicles and equipment systems (see 6.5).

2. SALIENT CHARACTERISTICS.

2.1 Material. The B20 shall consist of biodiesel (see 6.3.1) conforming to the requirements of ASTM D 6751 and diesel fuel oil conforming to A-A-52557 or ASTM D 975. The amount of biodiesel shall be 20 ± 1% by volume. The remainder of the fuel blend shall be Grade Low Sulfur No. 1-D diesel fuel oil (see 6.3.2), Grade Low Sulfur No. 2-D diesel fuel oil (see 6.3.3), or a combination of Grade No. 1-D and Grade No. 2-D.

2.2 Chemical and physical requirements. The chemical and physical requirements of the finished fuel shall conform to those listed in table E-1.

Beneficial comments, recommendations, additions, deletions, clarifications, etc. and any data that may improve this document should be sent by letter to: U.S. Army Tank-automotive and Armaments Command, ATTN: AMSRD-TAR-E/ASI, 6501 E. 11 Mile Road, Warren, MI 48397-5000. AMSC N/A FSC 9140 DISTRIBUTION STATEMENT A. Approval for public release; distribution is unlimited.

TABLE E-1. Requirements for B20 biodiesel blend.

Property	Requirement	Test Method
Volume percent biodiesel in B20	20 ± 1 volume percent	Appendix A
Appearance	Clear, bright, and visually free from undissolved water, sediment, and suspended matter	ASTM D 4176 Procedure 1
Kinematic Viscosity, mm^2/s, @ 40°C	1.3 – 4.1	ASTM D 445
Flash Point, °C April – September October – March	52°C min 38°C min	ASTM D 93
Low Temperature Properties	1/	1/
Total Acid Number, mg KOH/g Sample	0.2 max	ASTM D 664
Water Content, volume %	0.05 max	ASTM D 2709
Sulfur Content, mass %	0.05 max	ASTM D 5453, D 2622
Cetane Number	41 min	ASTM D 613
Ash Content, mass %	0.01 max	ASTM D 482
Distillation, °C T90	338 max	ASTM D 86
Copper Strip Corrosion, 3 hours @ 50°C	3 max	ASTM D 130
Micro Carbon Residue, mass %	0.05 max	ASTM D 4530

1/ The low temperature performance of the B20 shall be defined by one of the following two properties: cloud point or cold filter plugging point (CFPP). When specified (see 6.2), the maximum cloud point of the B20 shall be equal to or lower than the tenth percentile minimum ambient temperature in the geographical area and seasonal timeframe in which the B20 is to be used, when tested IAW ASTM D 2500. When specified (see 6.2), the maximum CFPP of the B20 shall be a minimum of 10°C below the tenth percentile minimum ambient temperature in the geographical area and seasonal timeframe in which the B20 is to be used, when tested IAW ASTM D 6371 (see 6.4). ASTM D 5773 can be used as an alternate cloud point test method to ASTM D 2500.

3. REGULATORY REQUIREMENTS. The offeror/contractor is encouraged to use recovered materials to the maximum extent practicable, IAW paragraph 23.403 of the Federal Acquisition Regulation (FAR).

3.1 Clean Air Act requirements. Under authority of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) issues limits on the maximum sulfur level, the maximum aromatic content or minimum cetane index on diesel intended for on-road use. Details of the EPA regulations and test methods are given in Part 80 of Title 40 of the Code of Federal Regulations

A-A-59693A 3

(40 CFR 80). Specifics may be obtained by contacting the Air Quality Office of the state environmental office or headquarters.

3.2 Legal requirements. B20 furnished under this description shall meet all applicable legal requirements in accordance with (IAW) 40 CFR 80.

4. PRODUCT CONFORMANCE. The products provided shall meet the salient characteristics of this CID, conform to the producer's own drawings, specifications, standards, and quality assurance practices, and be the same product offered for sale in the commercial marketplace. The Government reserves the right to require proof of such conformance.

5. PACKAGING. Preservation, packing, and marking shall be as specified in the contract or order (see 6.2).

6. NOTES.

6.1 Source of documents.

6.1.1 Copies of 40 CFR 80 are available from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402, or via the GPO website at http://www.access.gpo.gov/nara/cfr/index.html/ .

6.1.2 Copies of A-A-52557 "Fuel Oil, Diesel; for Posts, Camps and Stations" are available from the Document Automation and Production Service, Bldg. 4D, 700 Robbins Avenue, Philadelphia, PA 19111-5094 or via website http://assist2.daps.dla.mil/quicksearch/

6.1.3 Copies of the following ASTM documents can be obtained from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, or via the ASTM website at http://www.astm.org/

Table E-2. ASTM Test Methods

D 86	-	Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure (DoD Adopted)
D 93	-	Standard Test Methods for Flash-Point by Pensky-Martens Closed Cup Tester (DoD Adopted)
D 130		Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test (DoD Adopted)
D 445	-	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity) (DoD Adopted)
D 482	-	Standard Test Method for Ash from Petroleum Products (DoD Adopted)
D 613	-	Standard Test Method for Cetane Number of Diesel Fuel Oil (DoD Adopted)
D 664	-	Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration (DoD Adopted)
D 975	-	Standard Specification for Diesel Fuel Oils (DoD Adopted)
D 2500	-	Standard Test Method for Cloud Point of Petroleum Products (DoD Adopted)
D 2622	-	Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry (DoD Adopted)
D 2709	-	Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge (DoD Adopted)
D 4176	-	Standard Test Method for Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection Procedures) (DoD Adopted)
D 4530	-	Standard Test Method for Determination of Carbon Residue (Micro Method) (DoD Adopted)
D 4865	-	Standard Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems (DoD Adopted)
D 5453	-	Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence
D 5773	-	Standard Test Method for Cloud Point of Petroleum Products (Constant Cooling Rate Method)
D 6371	-	Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels (DoD Adopted)
D 6751	-	Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels

6.1.4 Copies of SAE Paper No. 1999-01-3520 "Potential Analytical Methods for Stability Testing of Biodiesel and Biodiesel Blends" can be obtained from the Society of Automotive Engineers (SAE), 400 Commonwealth Drive, Warrendale, PA 15096-0001, or via the SAE website at http://www.sae.org/ .

6.2 Ordering data. The contract or order should specify the following:

a. CID document number and revision.
b. Product conformance provisions.
c. Cloud point or CFPP required.
d. Quantity in terms of gallons or barrels bulk or number and size of containers for packaged lots.
e. Selection of applicable packaging or delivery requirements.

6.3 Definitions.

6.3.1 Biodiesel. A fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

6.3.2 Grade Low Sulfur No. 1-D. A special-purpose, light distillate fuel used for automotive diesel and gas turbine engines requiring low sulfur fuel and requiring a higher volatility than that provided by Grade Low Sulfur No. 2-D.

6.3.3 Grade Low Sulfur No. 2-D. A general-purpose, middle distillate fuel used for automotive diesel and gas turbine engines requiring low sulfur fuel. It is also suitable for use in non-automotive application, especially in conditions of varying speed and load.

6.4 Minimum ambient temperatures. Tenth percentile minimum ambient temperatures for locations within the United States are provided in Appendix X4 of ASTM D 975 and may be used as a means of estimating expected regional temperatures.

6.5 Limitations for B20 usage.

6.5.1 Vehicles and equipment. B20 has not been approved for use in Army combat and tactical vehicles and equipment at this time. The different types of engine systems and engine compartment configurations, modes of operation, environmental conditions, storage stability concerns (see 6.5.2), solvency effects (see 6.6), and fuel interchangeability issues associated with the single fuel forward policy will necessitate field testing to fully validate the use of B20 in combat and tactical vehicles and equipment.

6.5.2 Storage life. Available data indicates that the B20 in vehicles or storage tanks should be used within six months of manufacture. Fuels that have an acid number equal to or over 0.3 mg KOH/g are not recommended for use.

6.6 Solvency properties of biodiesel. Biodiesel (B100) is a good solvent. Use of B20 may clean the fueling system of existing deposits. Users should be prepared to change fuel filters more frequently upon initial use.

6.7 Viscosity and distillation properties of B20 blended with Grade No. 1-D diesel fuel oil. The user must be aware that B20 using Grade Low Sulfur No. 1-D diesel fuel oil as base fuel may exceed the maximum viscosity and the maximum 90% recovered temperature requirements for

Grade Low Sulfur No. 1-D diesel fuel oil IAW A-A-52557 and ASTM D 975. The significance of this deviation has not been established.

6.8 Static electricity. The generation of static electricity can create problems in the handling of distillate fuel oils with which biodiesel may be blended. For more information on the subject, see ASTM D 4865.

6.9 Original Equipment Manufacturers (OEM) biodiesel allowances. The impact of biodiesel use on warranty coverage, which varies by vehicle/engine manufacturers, has been checked. Major engine manufacturers have all issued statements regarding the use of biodiesel as it pertains to their warranty coverage. Copies of any of these statements can be obtained from the National Biodiesel Board (NBB) by calling (800) 841-5849 or faxing (573) 635-7913, or via the NBB website at http://www.biodiesel.org/

6.10 Benefits of using biodiesel. The Energy Conservation Reauthorization Act (ECRA) of 1998, an amendment to the Energy Policy Act (EPACT) of 1992, permits Federal Agencies to use biodiesel to meet a portion of their alternative fueled vehicle (AFV) acquisition requirements. Section 312 (Biodiesel Fuel Use Credits) of ECRA permits Federal Agencies to meet up to 50% of their AFV acquisition requirements by using biodiesel fuel. Under the new provisions, each 450 gallons of pure biodiesel (B100) used in a vehicle weighing over 8500 pounds counts as one full AFV credit. Since biodiesel is typically used as B20, using 2250 gallons of B20 equates to one AFV credit under EPACT.

6.11 Key words.

Blend
Compression ignition engine
Diesel consuming equipment
Low sulfur

VOLUME PERCENT BIODIESEL DETERMINATION IN A BIODIESEL BLEND BY GAS CHROMATOGRAPHY

1. Scope

1.1 This method covers the determination of biodiesel volume percent (throughout the test method volume percent is represented as %) in a blend of diesel fuel and biodiesel. The test method is applicable to fuel blends having 0 to 30% biodiesel. This method is not dependant on the type of biodiesel feedstock or the grade of diesel fuel used in the biodiesel blends.

1.2 This test method does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Summary of Test Method

2.1 A fuel sample is injected into a non-polar gas chromatographic column and run at specific conditions. The components of the biodiesel blend elute in boiling point order, with the biodiesel being the heaviest component. The initial column temperature is started high to elute the petroleum diesel quickly. Once the petroleum diesel has been eluted, the column temperature is raised to get good separation of the biodiesel components. A calibration curve is obtained under the same chromatographic conditions using known blends of biodiesel/petroleum diesel ranging from 0 to 30% biodiesel.

3. Significance and Use

3.1 This test method is useful in determining whether a fuel contains biodiesel and what volume percent of the blend is biodiesel. This method does not give any insight into the composition of the biodiesel feedstocks or of the grade of petroleum diesel used in the blend. This test method can be used for product specification testing of B20 fuel samples.

4. Apparatus

4.1 Gas Chromatograph. The gas chromatograph used must have the following performance characteristics:

4.1.1 Detector. A flame ionization detector (FID) capable of operating at 300°C and be capable of the connection of a megabore capillary column.

4.1.2 Column Temperature Programmer – The gas chromatograph must be capable of programmed temperature operation.

4.1.3 Sample Inlet System – The sample inlet must be capable of operating at 300°C and be capable of the connection of a megabore capillary column.

4.1.4 Flow Controllers – The gas chromatograph must be equipped with mass flow controllers capable of maintaining the carrier gas flow constant to ± 1% over the full operating temperature range of the column.

4.1.5 Microsyringe – A microsyringe capable of 0.1microliter (μL) volumes is needed for sample introduction.

4.2 Column – 5 meters (m) × 0.53 millimeters (mm) × 2.65 micrometer (µm) HP-1, Agilent Technologies, Part# 19095S-100 has been used with success.

4.3 Data Acquisition System

4.3.1 Integrator – Means must be provided for determining the accumulated area under the chromatogram. This can be done by means of an electronic integrator or computer-based chromatography data system. The integrator/computer system must have chromatographic software for measuring the retention time and areas of eluting peaks.

5. Reagents and Materials

5.1 Carrier Gas – Helium of high purity. (Warning – Helium is a gas under high pressure.) Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure must be sufficient to ensure a constant carrier gas flow rate.

5.2 Hydrogen – Hydrogen of high purity is used as fuel for the flame ionization detector (FID). (Warning – Hydrogen is an extremely flammable gas under high pressure.)

5.3 Air – High purity compressed air is used as the oxidant for the FID. (Warning – Compressed air is a gas under high pressure and supports combustion.)

5.4 Standards for Calibration and Identification – Standards of biodiesel and petroleum diesel are needed for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be free of the other components to be analyzed (i.e., the biodiesel shall be 100% biodiesel and the diesel fuel shall be 100% petroleum diesel fuel).

6. Sampling

6.1 Samples to be analyzed by this test method must be obtained using the procedures outlined in ASTM Practice D 4057.

6.2 The test specimen to be analyzed must be homogeneous and free of dust or undissolved material.

7 Preparation of Apparatus

7.1 Chromatograph – Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1.

7.1.1 Regularly remove the deposits formed in the flame ionization detector from the combustion of the silicone liquid phase decomposition products. These deposits will change the response characteristics of the detector.

7.2 Capillary Column – Capillary columns with cross-linked and bonded stationary phases are available from many manufacturers and usually require conditioning. The column can be conditioned using the following procedure.

7.2.1 Properly install the capillary column into the gas chromatograph at the inlet only. Cap off the detector and set the column flow. Allow the column to purge at ambient temperature for 30 minutes.

7.2.2 At the end of the column purge time, uncap the detector and install the capillary column to the detector and set the detector flows.

7.2.3 Starting at ambient temperature, ramp the oven 10°C per minute to the final operating temperature of 240°C and hold for 30 minutes.

7.2.4 Run the temperature ramp program until a stable baseline is obtained.

TABLE E-3. Typical operating conditions.

Column Length	5 m
Column inner diameter	0.53 mm
Film thickness	2.65 µm
Stationary phase	HP-1
Carrier Gas	Helium
Carrier gas flow rate	8.0 mL/min
Split Ratio	5:1
Initial Column temperature	170°C, Hold 8 minutes
Final Column Temperature	240°C, Hold 5 minutes
Programming rate	10°C/min
FID Hydrogen Flow	30 mL/min
FID Air Flow	400 mL/min
FID Makeup Flow	22 mL/min
Detector Temperature	300°C
Injector Temperature	300°C
Sample Size	0.1 µL
Data Rate	0.5 or 1 Hz
Total Analysis Time	20 minutes

8. Calibration and Standardization

8.1 Identification – 100% biodiesel (B100) contains three (3) major peaks. Determine the retention times and the percent concentration of each peak by injecting a 0.1µL sample. Figure 1 shows an overlay of 100% soy biodiesel fuel and 100% yellow grease biodiesel fuel samples. Notice that there is very little difference between the two B100 samples, so either fuel may be used for calibration.

8.2 Preparation of Calibration Blends.

8.2.1 Cal STD 1 – In a 100 mL volumetric flask, blend 30 mL of B100 (100% biodiesel) stock and dilute to the mark with biodiesel free petroleum diesel and label flask. This is the 30% biodiesel standard.

8.2.2 Cal STD 2 – In a 100 mL volumetric flask, blend 25 mL of B100 stock and dilute to the mark with biodiesel free petroleum diesel and label flask. This is the 25% biodiesel standard.

8.2.3 Cal STD 3 – In a 100 mL volumetric flask, blend 20 mL of B100 stock and dilute to the mark with biodiesel free petroleum diesel and label flask. This is the 20% biodiesel standard.

8.2.4 Cal STD 4 – In a 100 mL volumetric flask, blend 15 mL of B100 stock and dilute to the mark with biodiesel free petroleum diesel and label flask. This is the 15% biodiesel standard.

8.2.5 Cal STD 5 – In a 100 mL volumetric flask, blend 10 mL of B100 stock and dilute to the mark with biodiesel free petroleum diesel and label flask. This is the 10% biodiesel standard.

8.2.6 Cal STD 6 – In a 100 mL volumetric flask, blend 5 mL of B100 stock and dilute to the mark with biodiesel free petroleum diesel and label flask. This is the 5% biodiesel standard

8.2.7 Cal STD 7 – In a 100 mL volumetric flask, dilute to the mark with biodiesel-free petroleum diesel and label flask. This is the 0% biodiesel standard.

8.3 Standardization – Run the calibration standards and establish a calibration curve for each of the three biodiesel peaks. Using the concentrations of each peak obtained in section 8.1, calculate the value of each peak in each standard. Check that the correlation r^2 value for each calibration is at least 0.99 or better. Figure 2 shows an example of a Least-Squares Fit Calibration for biodiesel peak 2 as done by ChemStation software. To do a manual Least-Squares Fit Calibration see section 10, Calculations and Reporting.

TABLE E-4. Concentrations of standards.

Peak #	B100	30% Std	25% Std	20% Std	15% Std	10% Std	5% Std	0% Std
1	10.4%	3.120	2.600	2.080	1.560	1.040	0.520	0.000
2	85.1%	25.530	21.275	17.020	12.765	8.510	4.255	0.000
3	4.5%	1.350	1.125	0.900	0.675	0.450	0.225	0.000
Total %	100.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0

9. Procedure

9.1 Sample Preparation – If using an automatic sampler then transfer an aliquot of the sample into a glass gas chromatographic (GC) vial. Seal the GC vial with a Teflon-lined septum cap.

9.2 Chromatographic Analysis – Introduce a representative aliquot of the sample into the gas chromatograph using the same technique and sample size used for the calibration analysis. An injection volume of 0.1µL with a 5:1 split ratio has been used successfully. Start the recording and integrating devices in synchronization with the sample introduction. Obtain a chromatogram and an integrated peak report which displays the retention times and integrated area of each biodiesel peak.

9.3 Integration – Table 3 shows an example of integration events. The peak area before the three biodiesel peaks are summed, this is the petroleum diesel fuel. Each of the three biodiesel peaks are integrated individually and the three are summed to obtain the total % of biodiesel present in the sample.

Table E-5. Example of integration events.

Time	Integration Events	Value
Initial	Slope Sensitivity	25
Initial	Peak Width	0.4
Initial	Area Reject	1000
Initial	Height Reject	25
Initial	Shoulders	OFF
0.100	Area Sum	ON
5.900	Area Sum	OFF
12.200	Integration	OFF

10. Calculations and Reporting

10.1 Calculate the Least-Squares Fit calibration for each of the three biodiesel peaks using the following formulas:

Correlation = $(xy)\Sigma^2 / (\Sigma x^2)(\Sigma y^2)$ (1)
Slope = $\Sigma xy / x\Sigma^2$ (2)
Y-Intercept = y – (Slope × x) (3)
Where:
x_i = % Concentration of Standard
y_i = Peak Area
x = the Sum of x_i divided by the number of Standards
y = the Sum of y_i divided by the number of Standards
$x = x_i - x$
$y = y_i - y$
$xy = x \times y$
$x^2 = x \times x$
$y^2 = y \times y$

10.1.1 Table E-6 gives an example of the calculations for biodiesel peak #2. Using Equations (1), (2), and (3), the correlation r^2, slope, and y-intercept are calculated as follows:

r^2 = 2062123967630.830 / (506.941 × 4068495595.089) = 0.9998
Slope = 1436009.738 / 506.941 = 2832.6977
y-intercept = 36643.914 – (2832.6977 × 12.765) = 484.5286

10.1.2 The calculations can be checked by calculating the areas of the standards as unknowns using Equation (4) and the peak areas from Table E-6. The calculated % Concentration will closely match the actual concentration as seen in the following example:

% Concentration = ((0.00000 - 484.5286) / 2832.6977) × 0.9998 = -0.171
% Concentration = ((12763.0 - 484.5286) / 2832.6977) × 0.9998 = 4.334
% Concentration = ((24663.2 - 484.5286) / 2832.6977) × 0.9998 = 8.534
% Concentration = ((37027.6 - 484.5286) / 2832.6977) × 0.9998 = 12.898
% Concentration = ((49040.7 - 484.5286) / 2832.6977) × 0.9998 = 17.138
% Concentration = ((60402.6 - 484.5286) / 2832.6977) × 0.9998 = 21.149
% Concentration = ((72610.3 - 484.5286) / 2832.6977) × 0.9998 = 25.457

10.2 Each of the three biodiesel peaks for the unknown sample are calculated using the corresponding Least-Squares calibration using the following formula:

% Concentration = ((Peak Area – Y-Intercept) / Slope) × Correlation (4)

10.3 Add the % concentrations of each of the three biodiesel peaks for total biodiesel in the sample. Report the total volume percent to the nearest 0.01 volume percent.

Table E-6. Example calculation of correlation coefficient.

Biodiesel Peak 2

X_i	Y_i	x	y	xy	x^2	y^2
(% Conc.)			(Peak Area)			
0.000	0.000	-12.765	-36643.914	467759.566	162.945	1342776454.179
4.255	12763.000	-8.510	-23880.914	203226.581	72.420	570298067.122
8.510	24663.200	-4.255	-11980.714	50977.939	18.105	143537514.796
12.765	37027.600	0.000	383.686	0.000	0.000	147214.727
17.020	49040.700	4.255	12396.786	52748.323	18.105	153680296.046
21.275	60402.600	8.510	23758.686	202186.415	72.420	564475146.870
25.530	72610.300	12.765	35966.386	459110.914	162.945	1293580901.349

x y

12.765 36643.914 1436009.738 506.941 4068495595.089

$\Sigma xy = 1436009.738$

$(xy)\Sigma^2 = 2062123967630.830$

$\Sigma x^2 = 506.941$

$\Sigma y^2 = 4068495595.089$

11. Precision and Bias

11.1 Precision – The precision of this test method has not been determined by a statistical examination by interlaboratory test results.

11.2 Repeatability – The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials have not been determined.

Appendix F

Recommended Specification Sheet for B20

1.0 **SCOPE:** This specification covers a biodiesel fuel (B20) blend containing 20% biodiesel, with the remainder being CARB ultra low sulfur petroleum diesel.

2.0 **APPLICABLE DOCUMENTS:** Specifications and standards referenced in this document in effect on the opening of the invitation for bid forms a part of this specification.

3.0 **Requirements:**

3.1 **Material:**
The biodiesel blend shall consist of 20.0 +0/-2.0 % by volume, measured per
EN 14078. The remainder of the fuel shall be ultra low sulfur No. 1-D diesel fuel, ultra low sulfur No. 2-D diesel fuel, or combination of grade No.1 and grade No. 2-D diesel fuel. The petroleum diesel fuel used for the blending shall meet or exceed the requirements of the latest version of ASTM D975 and be approved by CARB. The biodiesel fuel used for blending process shall meet or exceed the requirements of the latest version of ASTM D6751 plus the cold flow filterability limits adopted in the June 2008 ASTM meeting.

Finished biodiesel fuel blends shall meet or exceed the specifications set forth by ASTM International in the latest version of " Standard Specifications for Diesel Fuel Oils D 975", including the changes adopted at the June 2008 ASTM meeting

The final blend B20 furnished shall be thoroughly mixed prior to delivery, such that it does not separate over time.

3.2 **Chemical and Physical Properties:**
The chemical and physical requirements of the finished fuel shall meet the requirements of the California Code of Regulations, Title 13, section 2281 (sulfur content) and section 2282 (aromatic content).
The appearance of the final blend B20 shall be clear, bright, and visually free from un-dissolved water, sediment, and suspended matter. Testing shall be as per ASTM D 4176 Procedure 1 Test Method.
The biodiesel portion meeting the requirements of ASTM D6751 shall contain less than10% aromatics and shall have Cetane number greater than 53.

The B20 shall meet the cloud point limits specified in ASTM section X4 and the Oxidation Stability test (EN 14112) in the adopted ASTM specification.

3.3 Storage Life:
Biodiesel (B20) fuel shall not deteriorate in ordinary storage and shall not form excessive gum, resin, or deposits in diesel during storage.

4.0 Quality Assurance Provisions:

4.1 The delivered product may be inspected and tested according to ASTM standards for Sulfur, and Aromatics and other test methods specified in ASTM D975 and ASTM D6751, including but not limited to Cloud Point, Acid Number, Total and Free Glycerin.

4.2 Supplier shall provide the Certificate of Analysis for properties of blended biodiesel including but not limited to Cloud Point, Acid Number, Total and Free Glycerin.

4.3 B20 blend shall conform to latest recommendations / specifications of the ATSM specification for B20 that was passed during the June 2008 ASTM meeting.

4.4 Producer of biodiesel shall be most preferably be accredited to BQ -9000. (This is because some areas might not have BQ-9000 suppliers.)

Appendix G –

Recommended Best Practices When Converting to Biodiesel

Technical Recommendations for B20 Fleet Use Based on Existing Data
B20 Fleet Evaluation Team: June 2005

Biodiesel is the pure, or 100 percent, biodiesel fuel. It is referred to as B100 or "neat" biodiesel.

A biodiesel blend is pure biodiesel blended with petrodiesel. Biodiesel blends are referred to as BXX. The XX indicates the amount of biodiesel in the blend (i.e., a B20 blend is 20 percent by volume biodiesel and 80 percent by volume petrodiesel).

Ensure the biodiesel meets the ASTM specification for pure biodiesel (ASTM D 6751) before blending with petrodiesel. Purchase biodiesel and biodiesel blends only from companies that have been registered under the BQ-9000 fuel quality program.

Ensure the B20 blend meets properties for ASTM D 975, Standard Specification for Diesel Fuel Oils or the ASTM specification for B20 once it is approved.

Ensure your B20 supplier provides a homogenous product.

Avoid long term storage of B20 to prevent degradation. Biodiesel should be used within six months.

Prior to transitioning to B20, it is recommended that tanks be cleaned and free from sediment and water. Check for water and drain regularly if needed. Monitor for microbial growth and treat with biocides as recommended by the biocide manufacturer. See the NREL Biodiesel Storage and Handling Guidelines for further information http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/tp36182.pdf.

Fuel filters on the vehicles and in the delivery system may need to be changed more frequently upon initial B20 use. Biodiesel and biodiesel blends have excellent cleaning properties. The use of B20 can dissolve sediments in the fuel system and result in the need to change filters more frequently when first using biodiesel until the whole system has been cleaned of the deposits left by the petrodiesel.

Be aware of B20's cold weather properties and take appropriate precautions. When operating in winter climates, use winter blended diesel fuel. If B20 is to be used in winter months, make sure the B20 cloud point is adequate for the geographical region and time of year the fuel will be used.

Perform regularly scheduled maintenance as dictated by the engine operation and maintenance manual. If using B20 in seasonal operations where fuel is not used within 6 months, consider storage enhancing additives or flushing with diesel fuel prior to storage.

These recommendations on use of B20 are preliminary and are not provided to extend or supplant warranty limitation provided by an individual engine or equipment supplier. Use of B20 blends is solely at the discretion and risk of the customer and any harm effect caused by the use of B20 are not the responsibility of the engine or equipment maker.

Appendix H –

Example of a Caltrans Electronic Maintenance Record

Shop	Work Order Year	Work Order #	Task Code	Task Description	Job Reason	Meter 1	Date Closed	Commercial Total	Internal Parts Total	Commercial Parts Cost	Internal Labor	Job Total
28311	2006	1	699-503	ROAD TEST (BEORE OR AFTER REPAIRS)	11	176141	09-Jan-06	0	0	0	0.5	18.25
28311	2006	1	045-021	ELECTRONIC ENGINE CONTROLS	11	176141	09-Jan-06	0	0	0	1	36.5
		1 Total						0	0	0	1.5	54.75
28310	2006	84	002-017	CAB DOOR	11	176141	21-Mar-06	0	0	0	1.5	54.75
28310	2006	84	003-002	SPEEDOMETER	11	176141	21-Mar-06	0	0	0	1	36.5
28310	2006	84	699-500	SAFETY INSPECTION	11	176141	21-Mar-06	0	0	0	1	36.5
28310	2006	84	699-501	EQUIPMENT TRANSPORT OR TOW	11	176141	21-Mar-06	0	0	0	3	109.5
		84 Total						0	0	0	6.5	237.25

Appendix I –

Caltrans Indio Biodiesel Driver Survey

1. Does the vehicle experience any problems starting? How does the startability with biodiesel compare with that of diesel fuel? (circle one)

   none   similar to diesel   better than diesel   worse than diesel

2. Does the vehicle experience any problems with driveability? How does the driveability with biodiesel compare with that of diesel fuel? (circle one)

   none   similar to diesel   better than diesel   worse than diesel

3. What is your perception of the odor of the exhaust from the biodiesel? (circle one)

   none   similar to diesel   better than diesel   worse than diesel

4. How does the power level of the vehicle on biodiesel compare to the power level on diesel fuel? (circle one)

   similar to diesel   better than diesel   worse than diesel

5. How does the power level of the vehicle on biodiesel compare to the power level on diesel fuel? (circle one)

   similar to diesel   better than diesel   worse than diesel

6. Have you experienced any driving problems with the use of the biodiesel fuel in comparison with that of the diesel fuel?

   ____

7. Do you see any difference in the power levels at higher loads, such as climbing a hill or accelerating on the freeway?

   ____

8. Have you experienced any problems starting the vehicle on cold mornings or after the vehicle sits for longer periods of time?

   ____

9. Have you experienced any fueling problems with the use of the biodiesel fuel in comparison with that of the diesel fuel?

   ____